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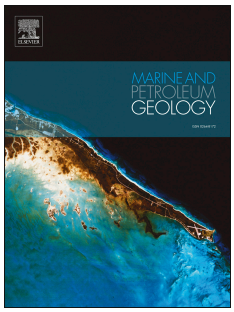

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CRediT authorship contribution statement

M.S. designed the project, analysed the data and wrote the manuscript. This study is partly based on S.S.'s BSc thesis (Słama, 2019) supervised by M.S., which provided some biomarker analyses. J.G. provided oil samples. A.K. performed the GC-FID and GC-MS. T.E. and P.S. provided seismic and geological data and oil samples. J.G., S.S., M.M., M.E.T., I.P. contributed to writing the article. All authors approved the manuscript.

A new and working petroleum source rock on the UK Continental Shelf (Upper Permian, offshore Yorkshire)

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Abstract

We report on the discovery of oil from the Boulby Mine and its likely productive source rock from Yorkshire in NE England, located to the west (<30 km) of the newly licenced petroleum exploration areas in the vicinity of the Mid-North Sea High. Oil samples from the mine have likely been generated from Zechstein Group Kirkham Abbey Formation (KAF) sapropelic carbonate rock as indicated by aliphatic and aromatic hydrocarbon biomarkers. Other potential source rocks of Carboniferous (Westphalian, Namurian, Viséan coals and mudrocks) and Jurassic (the Jet Rock, Bituminous Shales, Kimmeridge Clay Formation) age are ruled out on the basis of organic geochemical data. Boulby oil was generated in the peak-to-late oil-window and it is characterised by the high abundance of C_{32} and C_{34} homohopanes,

slight even-over-odd predominance (EOP) of C_{20-25} *n*-alkanes indicating restricted carbonate-evaporite depositional conditions, and C_{29} ethyl-diacholestane 20S likely implying a clay-rich source rock. The structural framework and tectonic history of the Permian strata reveal the presence of several fault systems which served as conduits for migrating petroleum. Similar Zechstein-sourced oil is known from Poland and Germany, but the occurrence at Boulby is the first positive identification of oil derived from Zechstein source rock in the North Sea area. The Boulby oil is reservoired in Zechstein 3 (Z3) Brotherton Formation dolomite and sealed by Z3 evaporite rocks. The proven oil occurrence at Boulby has significant implications in terms of reducing the risk of a lack of oil mature source rock for acreage offered in the neighbouring North Sea during the UK's 30th and 31st licencing rounds.

Keywords: seeping oil, source rock, Boulby Mine, Yorkshire, Zechstein, Late Permian

1. Introduction

The Boulby Mine opened in North Yorkshire, England, in 1973 (Woods, 1979, 1973) for the mining of halite, polyhalite and sylvite from strata of Late Permian (Zechstein cycle 2 [EZ2] and 3 [EZ3]) age. The sylvite was originally identified in a prospect drilled for oil by the D'Arcy Exploration Company in 1939 at Aislaby on the Eskdale Anticline. Well Eskdale 2 (Fig. 1), drilled a few km south of the present location of the mine, proved potash-bearing minerals within three cycles of the Zechstein evaporite succession (EZ2, EZ3 and EZ4).

The mine workings reach a depth of 1300 m below sea level and extend ~8 km towards and under the North Sea. The Boulby Mine is located in the Mesozoic Cleveland Basin of northeast England (Fig. 1), which is the onshore development of the Sole Pit Trough. It occurs on the margin of the Southern Permian Basin (SPB) of northwestern Europe, which later became the North Sea Basin, containing thick sedimentary (sandstone-carbonate-evaporite) sequences (Glennie and Underhill, 1998).

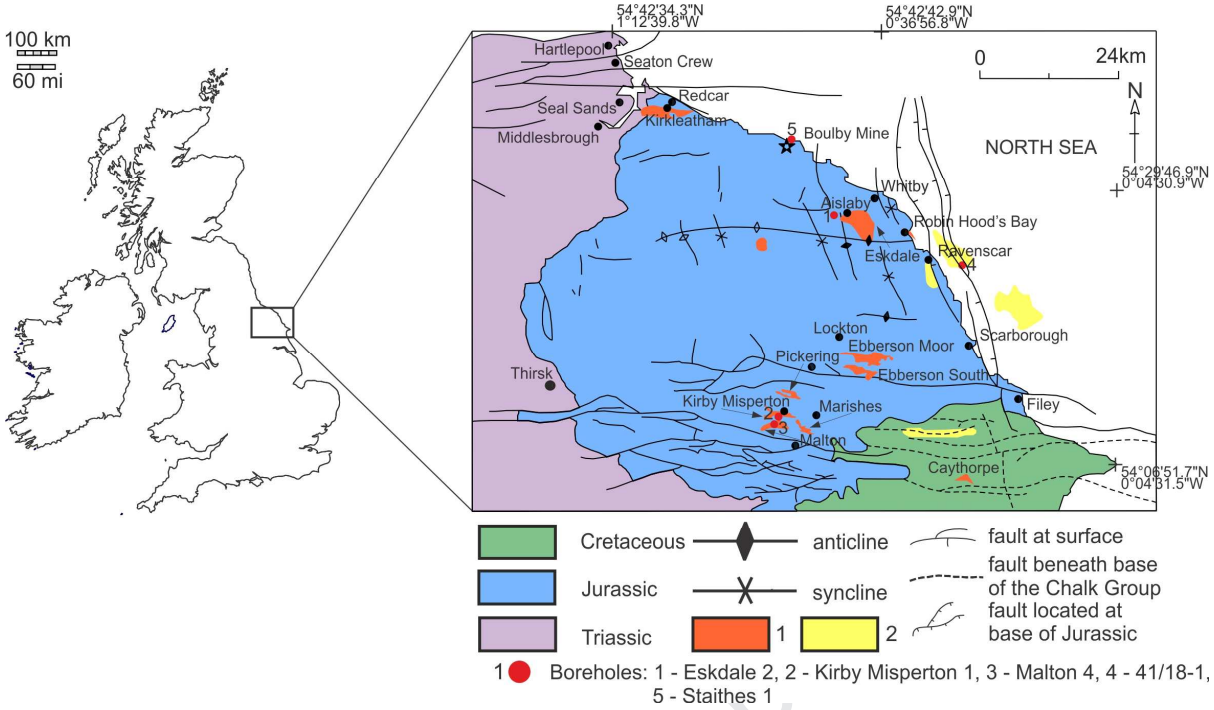


Fig. 1. Map of the Cleveland Basin and its major structural features indicating the position of the Boulby Mine (after Powell, 2010). The West Newton location is not shown and is ~113 km south of Boulby. 1 – gas fields; 2 – undeveloped gas discoveries (after Haarhoff et al., 2018).

In 2011, through fractures encountered during mining operations in a salt roadway and from an exploratory horizontal borehole drilled through the salt, a brine, oil and methane gas influx occurred. The origin of this seeping oil had been linked to the Carboniferous Coal Measures and terrigenous organic matter (OM) type (Davison, 2009). In the vicinity of the Boulby Mine, there are several gas fields (e.g., Eskdale, Lockton [now called Ebberson Moor], Malton, Marishes and Pickering; see Fig. 1, and the recent discovery at West Newton located ~113 km south of Boulby) hosted by Zechstein dolomites of the Kirkham Abbey (KAF) and Brotherton formations (EZ2 and EZ3, respectively; Fig. 2). Productive tests were reported from Namurian strata in the Kirby Misperton Field and from Rotliegend sandstone in the Caythorpe Field (also producing from the KAF) (Fig. 1). There have also been oil shows in a number of discoveries offshore of the Cleveland Basin (Quadrant 41), including well 41/18-1, just offshore of Robin Hood's Bay, and in KAF and Brotherton Formation carbonate rocks in the Teesside area close to the northern margin of the Cleveland Basin, including wells at Hartlepool and Seaton Carew (Smith and Francis, 1967 and references therein), as well as gas production at Kirkleatham (Fig. 1). It has long been assumed that the gas was generated from coal in the Upper Carboniferous interval. The Namurian source rock

present in the East Midlands and Liverpool Bay oil provinces has not been shown to be oil-prone in the North Yorkshire area (Andrews, 2013). Other potential candidate source rocks for the oil at Boulby Mine are Jurassic mudrock of the Lower Jurassic Jet Rock and Bituminous Shales and the Upper Jurassic Kimmeridge Clay Formation (KCF). Some oil seepage is known from septarian concretions within the Toarcian Jet Rock bituminous shale exposed on the coast above the mine (Fig. 3), but shale is only marginally mature (Kent, 1980; Rawson and Wright, 1995, 2018). Further south along the coast the KCF is present but thermally immature for petroleum. Boulby Mine is a considerable distance away (400 km) from the Tail End Graben in the Central North Sea where the KCF is mature for petroleum (Glennie et al., 2003).

To explore this conundrum and to test whether the Boulby oil was derived from Carboniferous, Jurassic or a different source-rock we have recently collected four seeping oil samples in a newly-opened part in the mine (2000 West Salt). Our new data include broader organic geochemical analyses of Boulby oil allowing a detailed determination of the OM source for the hydrocarbons, as well as the depositional conditions. We have quantified a suite of biomarker signatures characteristic of past redox conditions, including homohopane ratios, complemented by hopane and sterane distributions indicative of changes in OM source. These, as well as geological and tectonic interpretations, are used to refine the origin of the Boulby oil. These findings open a new window to petroleum exploration in the North Sea, particularly in terms of defining several new pods of active source rock.

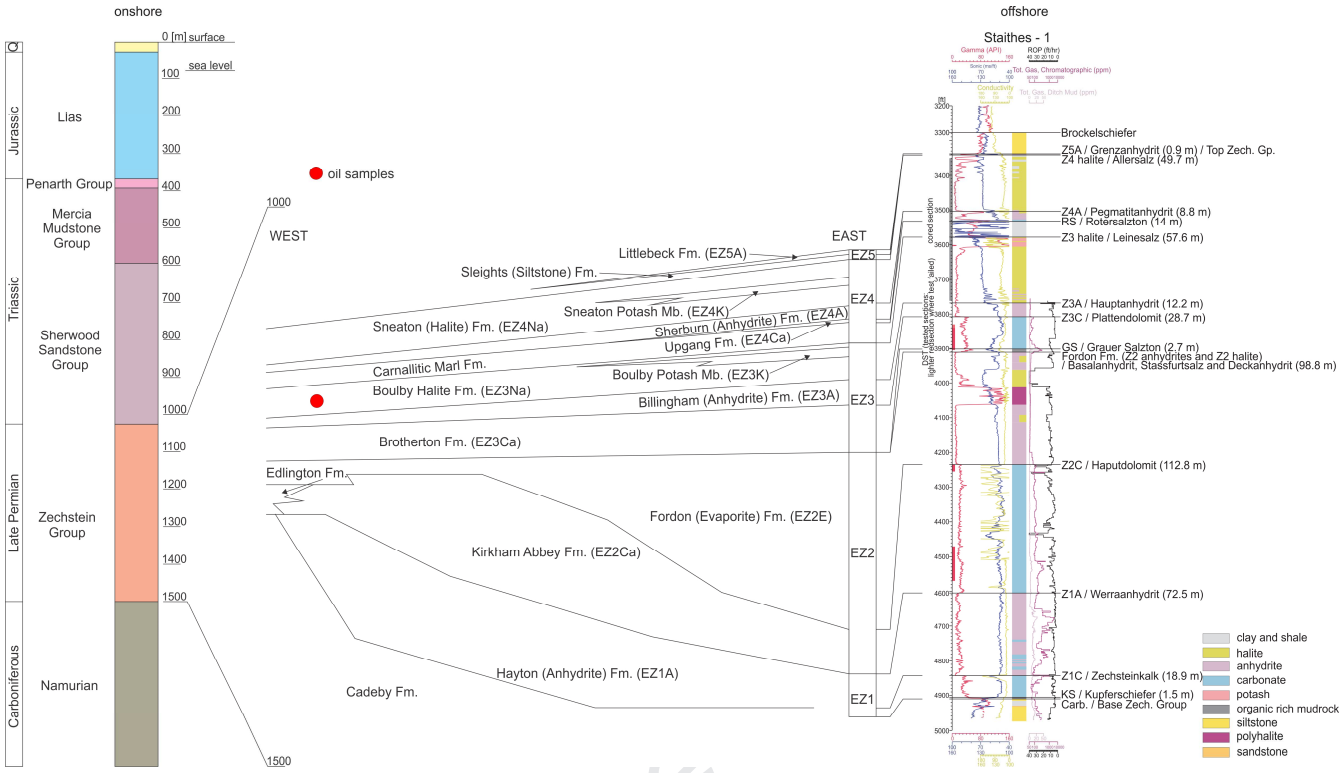


Fig. 2. Onshore (from the Boulby Mine) and offshore (well Staithes 1) stratigraphic correlation of the English Zechstein in NE Yorkshire (this paper and after Smith et al., 1986). Note the Chalk Group is absent in the Boulby area. EZ1-5 – English Zechstein cycles 1-5; Carb. – Carboniferous; Zech. Gp. – Zechstein Group.

Fig. 3. Oil seeping from a 'whalestone' concretion in Liassic bituminous mudstone at Port Mulgrave (photo courtesy of Jack Lee).

2. Geological setting

2.1. Stratigraphy

North Yorkshire and Cleveland Basin lithostratigraphy, modified after Kent (1980), is shown in Figure 2. The oldest rocks are mudstone and siltstone with carbonate beds (Lower Carboniferous, Craven Group, >760 m thick, comprising Bowland Shale Formation and Shale Limestone Unit), sandstone, mudstone and siltstone (Namurian Millstone Grit Group, 730 m thick) and a thick succession of Upper Carboniferous mudstone/siltstone with coal (Westphalian Coal Measures Group, 620 m thick, absent in the Boulby Mine area). Permian strata are Upper Rotliegend (Guadalupian) Yellow Sands (aeolian sandstone and breccia, although absent in the Boulby Mine area) and Zechstein evaporite and carbonate rocks (~400 m thick). The Zechstein Group consists of five cycles (EZ1-EZ5) containing thick halite and carbonate and thin anhydrite and potash units. Carbonate rocks comprise dolomites of the KAF (EZ2Ca = Hauptdolomit in the Southern North Sea, western SPB) and Brotherton Formation (EZ3Ca = Plattendolomit in western SPB). They are sealed by halite and anhydrite beds of the EZ1, EZ2 and EZ3 cycles. Zechstein rocks are overlain by the Triassic Sherwood Sandstone (350 m thick), Mercia Mudstone (320 m thick) and Penarth groups (20 m thick). Lower Jurassic (Lias Group shale, 435 m thick), Middle Jurassic and Upper Jurassic strata, which crop out extensively along the southern side of the Cleveland Basin and Quaternary sediments complete the stratigraphy in the Boulby area.

2.2. Basin development

Since the Late Palaeozoic the Cleveland Basin area has undergone two major phases of basin development (Holliday, 1999). The first of these was rapid burial in the Carboniferous terminated by the Variscan Orogeny at the end of the Carboniferous (Corfield et al., 1996). The second, more recent event developed throughout much of the Mesozoic, terminating with uplift in the Paleogene (Kent, 1980; Imber et al., 2014).

The Carboniferous interval in the Cleveland Basin is known only from a few boreholes drilled onshore for petroleum exploration (Malton 4, Kirby Misperton 1; Słowakiewicz et al., 2015), waste chemical disposal (Seal Sands near Hartlepool; Johnson et al., 2011; Andrews, 2013), and offshore for petroleum exploration in Quadrant 41 (Besly, 1998). The oldest strata penetrated belong to the Fell Sandstone Formation (Arundian = Viséan). The Fell

Sandstone Formation is known from outcrop further north in Northumberland to have been deposited in a high-energy fluvial system. It is overlain by a shale-dominated interval with subordinate sandstones and limestones deposited in paralic to shallow-marine conditions during a syn-rift episode (Fraser and Gawthorpe, 1990). Post-rift sediments are also largely paralic but with substantially more sandstone (Millstone Grit and Coal Measures groups). The maximum thickness of the Carboniferous interval is in excess of 3000 m (Imber et al., 2014). By the end of the Carboniferous the area of the current Cleveland Basin was undergoing inversion resulting from the Variscan Orogeny and this resulted in the removal of the Coal Measures Group over large areas so that the Permian strata commonly overstep Namurian and Dinantian rocks. Uplift and erosion of the Cleveland area lasted until the Early Permian when a second phase of rifting began.

By the Early Permian the area was within the single Pangea supercontinent and, although subsidence had lowered the basin surface below contemporaneous sea level, the area was not inundated. A land-locked basin developed with sedimentation occurring under aeolian, sabkha and ephemeral fluvial conditions to form the Yellow Sands Formation. This sandstone has been comprehensively described immediately north of the Cleveland Basin (but is absent in the Boulby Mine area) in County Durham where it crops out and where quarrying has afforded good exposure. The Yellow Sands Formation constitutes a series of NE-SW trending sand ridges up to 60 m high and 1.5 to 3.5 km wide, separated by areas up to 2 km wide that lack sand (Steele, 1983).

Sandstone deposition ended when the barrier to the Tethyan Ocean to the south east was breeched and the seaway to Panthalassa in the north opened up so that what had been a sub-sea-level basin dominated by deposition of terrestrial sediments became the Zechstein Sea.

The Late Permian was mostly a period of regional subsidence allowing up to many 100s m of carbonate and evaporite units of the Zechstein Group to be deposited (Smith, 1989; Taylor, 1998). These sediments form broadly off-lapping packages of carbonate and anhydrite, with one major phase of basin-filling halite (EZ2E, Fordon Formation evaporite = Stassfurt evaporites in the SPB). There is evidence in County Durham for some synsedimentary fault movements which controlled deposition of the EZ1Ca reef (Ford Formation = Zechstein Limestone in the SPB, Daniels et al., 2020).

The Mesozoic cover sequence in the area comprises Triassic and Jurassic sedimentary rocks, the youngest being Middle Jurassic at the surface across the North Yorkshire hills. Younger, Upper Jurassic rocks are exposed along the southern margin of the Cleveland Basin

(Powell, 2010), and, together with Cretaceous strata, crop out immediately south of the area of interest and would in the past have been part of the sedimentary cover at Boulby before Paleogene inversion. According to Holliday (1999) there was probably a thick succession of Chalk Group and Paleogene sediments present prior to Paleogene uplift and erosion.

The Triassic succession, divisible into a lower Sherwood Sandstone Group, an upper Mercia Mudstone Group and the Penarth Group, is still present in the subsurface. The likely original thicknesses of these strata are up to 685 m (350 m, 320 m, 15 m, respectively; Kent, 1980). The Sherwood Sandstone Group was predominantly deposited by braided fluvial systems and the overlying Mercia Mudstone Group sediments accumulated as playa lake deposits.

The Lower Jurassic strata of the Lias Group are up to 435 m thick and dominated by mudstone with subordinate sandstone and ironstone (Powell, 2010). The Redcar Mudstone Formation (256 m) occurs at the base and includes calcitic, siliceous and pyritic/ironstone marine shales. The shales are overlain by the Staithes Sandstone Formation (25 m) deposited below wave-base in marine conditions as storm beds (van Buchem and Knox, 1998). The youngest section of the Lower Jurassic Lias Group comprises the Whitby Mudstone Formation (107 m thick), which, near the base, in the Mulgrave Shale member, contains organic-rich mudrocks of the 8.5 m thick Jet Rock (equivalent to the Schistes Carton of the Paris Basin) and overlying 23 m of thick Bituminous Shales (Rawson and Wright, 1995, 2018).

The Middle Jurassic strata are the youngest rocks exposed in the vicinity of the Boulby Mine; they also crop out extensively in the Cleveland Basin and most comprise non-marine siliciclastics with minor coal of the up to 240 m thick Ravenscar Group (Powell, 2010). Deposition occurred in a range of paralic sub-environments, shallow-marine to delta-top. Younger Jurassic strata crop out towards the southern margin of the basin, ~30 km to the south of the Boulby Mine, and include the Oxford Clay, carbonate rock of the Corallian Group and, at the top of the preserved succession, the ~300 m thick KCF mudrock.

2.3. Inversion

The area of the Cleveland Basin has undergone two phases of inversion since the beginning of the Late Palaeozoic (Kent, 1980; Chadwick et al., 1993; Holliday, 1999). The Variscan Orogeny caused a regional phase of uplift at the end of the Carboniferous as the supercontinent Pangea came into existence. Uplift was substantial, causing on the order of

1.5 km of erosion as a minimum in the Cleveland area (Kent, 1980) and, offshore in Quadrant 42 (80 km east of Boulby), Lower Permian sediments overlie Devonian strata (Underhill, 2003). The Zechstein Group overlies Devonian rocks also in parts of Quadrant 38 (Taylor, 1998). This phase of uplift resulted in the removal of Coal Measures as a potential source rock, as well as the uplift of older source rocks, i.e., the Carboniferous Bowland Shale Formation mudrock.

A second phase of uplift occurred in the Late Cretaceous. In the Cleveland Basin an estimated 1 to 1.5 km of Upper Cretaceous to Upper Jurassic sediment was stripped off (Kent, 1980; Imber et al., 2014), leaving the Middle Jurassic paralic sediments as the youngest now seen in the area.

2.4. Candidate source rocks

In this section an overview of potential source rocks for Boulby oil in the Cleveland Basin is provided. These include Upper Jurassic KCF mudrock, Toarcian shale and coal, Zechstein lagoonal facies, Carboniferous Coal Measures, as well as Namurian and Viséan mudrocks.

2.4.1. Kimmeridge Clay Formation (KCF)

The organic richness of KCF mudrock (300 m thick) and the results of Rock-Eval pyrolysis show that the average total organic carbon (TOC) values are 5-8 wt.%; the quality of kerogen is excellent with respect to hydrocarbon generation, and the hydrogen index (HI) ranges from 500 to 600 mg HC/g TOC. In some places where there is an immature-mature transition the TOC and HI values reach 32 wt.% and 1200 mg/g TOC, respectively; sapropelic marine kerogen type II predominates (Scotchman, 1991). The $\delta^{13}C$ values of saturated and aromatic bitumen fractions range from -32 to -25 ‰ (Bailey et al., 1990; Cooper et al., 1995; van Kaam-Peters et al., 1997; Gautier, 2005).

The features of KCF source rock are a significant enrichment of C_{33-35} homohopanes (de Leeuw and Sinninghe Damsté, 1990), a high abundance of 28,30-bisnorhopane (Grantham et al., 1980; Peters et al., 1989), a dominance of C_{27} and C_{29} steranes (Mackenzie et al., 1983; Huc et al., 1985), and the presence of isorenieratene derivatives (van Kaam-Peters et al., 1997; Sinninghe Damsté et al., 2001).

2.4.2. Lower Jurassic mudrocks of the Jet Rock and Bituminous Shales

Lower and Middle Jurassic coals and shales are believed to contribute locally as petroleum sources (Husmo et al., 2002). Jet Rock and Bituminous Shales form part of the Mulgrave Shale Member at the base of the Whitby Mudstone Formation. The Jet Rock's equivalents in the Paris Basin (Schistes Carton) and Germany (Posidonienschiefer) are petroleum source rocks. The TOC content in Toarcian shale of Runswick Bay varies from 2.5 to 18.9 wt.%; HI ranges from 500 to 700 mg HC/g TOC, and kerogen type II is predominant (Song, 2015; Song et al., 2015). Vitrinite reflectance values are between 0.6 and 0.7 $\%R_o$ (Song, 2015; Song et al., 2015), indicating the early oil generation window. The $\delta^{13}C$ values of OM in the shale vary from -27.3 to -25 ‰ (Bailey et al., 1990).

2.4.3. Zechstein Group carbonate rocks

Kirkham Abbey Formation (KAF) carbonate rocks (Zechstein cycle 2, EZ2) in the Cleveland Basin area, which are sealed at the top and bottom by the Fordon Formation and Hayton Anhydrite evaporites, respectively, chiefly consist of ramp to slope facies (lagoonal, oolitic, turbiditic, pelagic, slump and debrite carbonate rocks), which extend landwards and interfinger with siliciclastic lagoonal-evaporitic facies of the Edlington Formation (Smith, 1989; Taylor, 1998). Clay- and microbial- rich lagoonal dolomites are, in addition to lower slope facies and chicken-wire anhydrites, regarded as source rocks for Zechstein oil in the central and eastern SPB (Słowakiewicz et al., 2018). Lagoonal carbonate facies in the Yorkshire area have TOC <2 wt.% and thickness ~25-35 m (Słowakiewicz et al., 2016). In addition, thinly-laminated basinal calcareous mudstone, named Stinkschiefer in the SPB, commonly regarded as a source rock for hydrocarbons, has previously been ruled out by Słowakiewicz and Gąsiewicz (2013) as an effective source rock. Furthermore, Zechstein cycle 3 (EZ3) Plattendolomit (= Brotherton Formation) representing ramp facies are only regarded as good reservoir rocks for petroleum in the North Sea (e.g., Wissey field located in the southern North Sea, Duguid and Underhill, 2010), although bituminous organic-rich limey mudstone of the Grauer Salzton Formation (the lowermost unit of the Plattendolomit) (Duguid and Underhill, 2010) might serve as a potential source rock. In addition, Zechstein lagoonal carbonates with anhydrite units may also be potential source rocks, with the OM derived from former microbial mats with clay.

2.4.4. Carboniferous Coal Measures Group

The Westphalian Coal Measures Group represents cyclic fluvio-deltaic sedimentation in a lower delta-plain environment at times when the influx of sand was at a minimum (Fraser and

Gawthorpe, 1990; Burgess and Gayer, 2000). The majority of Westphalian sandstone reservoirs are currently producing gas, which is sourced from Coal Measures with a possible contribution from Namurian basinal shales (Kombrink et al., 2010). Westphalian coal source rocks are largely absent from the Cleveland Basin (Haarhoff et al., 2018) due to Variscan uplift over wide areas prior to deposition of Permian sediments.

2.4.5. Namurian and Dinantian source rocks

Lower Carboniferous and Namurian source rocks are represented by black shale formed in marine deep-water basins and coal developed on terrigenous to marginal-marine delta plains (Fraser and Gawthorpe, 1990). Basinal shale alternating with carbonate beds was deposited on the slope of carbonate platforms and in the basinal areas. After carbonate sedimentation ceased (Namurian-Viséan transition) black shale was deposited across carbonate platforms (e.g., Bowland Shale Formation on the Derbyshire Block). In the basinal areas, black shale deposition continued from the Viséan into the Namurian (Pletsch et al., 2010).

Petroleum has been found in fractured Viséan shelf carbonates sourced by Namurian basinal shale at a number of locations in Derbyshire (Fraser and Gawthorpe, 1990; DECC, 2013). Highly mature Hardstoft oil (located south of Chesterfield, in eastern Derbyshire) is sourced from Viséan calcareous shale (Craig et al., 2015, and our unpublished biomarker data). Namurian and lower Westphalian (Langsettian) sandstone reservoirs host several oil and gas fields in the East Midlands, Gainsborough Trough and Yorkshire. In all cases the source rock is gas-prone Namurian basinal shale and Westphalian Coal Measures (Kombrink et al., 2010).

The Namurian Bowland Shale Formation of the Cleveland Basin has been identified as having substantial unconventional hydrocarbon resource potential (Andrews, 2013; Haarhoff et al., 2018). TOC of Bowland Shale Formation mudrock varies from 1.3 to 9.1 wt.%; the dominant kerogen is a gas-prone humic terrigenous type III, and the Carboniferous section is mature for gas generation in the Cleveland Basin (Hughes et al., 2018) and further south in the Pennine Basin (Gross et al., 2015).

In addition, in the Great Limestone Member (Namurian) Creaney et al. (1980) reported the presence of bitumen characterised by the predominance of low molecular weight *n*-alkanes in calcite veins. The Great Limestone Member belongs to the Yoredale Group, which comprises repeated sequences of limestone, shale, sandstone and coal. The average thickness

of these cycles is ~30 m (Chadwick et al., 1993), of which dark limestone, shale and coal might serve as a potential source rock for petroleum. Similarly, Edale oil (located southwest of Boulby, in northern Derbyshire) is sourced from the Edale Shale Group mudrock (= Bowland Shale Formation) of the lowermost Namurian (Fraser and Gawthorpe, 1990; Gluyas and Bowman, 1997). Also, in the Midland Valley of Scotland, Viséan Strathclyde Group oil shale is a rich source rock for petroleum (Underhill et al., 2008).

2.5. Distribution and perception of thermal maturity

Thermal maturity development in the Cleveland Basin is still poorly understood. According to Barnard and Cooper (1983) Carboniferous Coal Measures Group sediments have thermal maturity >2 % on the vitrinite reflectance scale (R_o), whereas Middle and Upper Jurassic rocks have R_o values from 0.3 % in southern part of the Cleveland Basin to 0.8 % in the Boulby area, also suggesting greater burial in the latter. Curiously, in the Malton area (Fig. 1) R_o is ~0.3 % in Jurassic rocks, but 20 km farther north at Lockton, R_o values increase (R_o 0.5-0.6 %), which might imply the influence of fault-related hydrothermal higher heat flow (Barnard and Cooper, 1983; Imber et al., 2014). Based on the illite-smectite assemblage Kemp et al. (2005) suggested burial depths of 4 km and a geothermal gradient of 25-30 ^{o}C/km for Lias shale. In addition, the Toarcian Whitby Mudstone Formation is in the early oil window (French et al., 2014), but the Carboniferous Bowland Shale-Hodder Mudstone shales are thermally mature for gas (Haarhoff et al., 2018). Higher thermal maturity (R_o ~0.8-0.9 %) has also been noted in Lockton 2a KAF limestone slope facies, revealed by negative $\delta^{18}O$ values (-2 to -14 ‰), the presence of saddle dolomite and increased abundance of tricyclic and tetracyclic terpenoids (Słowakiewicz et al., 2016).

3. Materials and methods

3.1. Sample collection

Four crude-oil samples (one Boulby black oil [sample 1] and three light-brown Boulby oil [samples 2-4] samples) dripping out of fractures in rock salt of the Boulby Halite Formation (EZ3Na, Figs 2,4) from the roof of the Boulby Mine at workings (2000 West Salt) at a depth of 1100 m subsurface were collected by hand into pre-furnaced glass jars. The glass jars were sealed with pre-furnaced aluminium foil and stored at 4 °C.

In addition, comparisons are made in this paper to previously published and reported herein biomarker data from fourteen samples of KAF dolomite lagoonal facies (onshore equivalent of the Innes Carbonate Member of the NPB) of the Malton 4 well (Słowakiewicz et al., 2016), and typical carbon isotopic values for saturated and aromatic fractions of Jurassic, Permian and Devonian oil from the SPB and North Sea areas.

3.2. 3D seismic data

A 3D seismic survey was undertaken by ICL UK Ltd in 2011 as part of an ongoing exploration programme for potash and polyhalite. The data reveal some interesting structural features which correlate with both the locations of the oil samples collected in this study and with previous instances of hydrocarbons in this specific area of the mine. Data for this survey were acquired by CGG and processed by Fugro. Interpretation was carried out by a combination of external contractors and on-site staff at the Boulby Mine.

3.3. Density determination of Boulby oil samples

Oil samples were analysed at 20 ^{o}C for API gravity using an Anton-Paar DMA^{TM} 5000 M density meter. A minimum of two replications were collected for each sample and the average value was used.

3.4. Extraction and biomarker analyses

Approximately 120 mg of the crude-oil samples were subjected to a fractionation procedure. Prior to this, asphaltenes were precipitated by adding 60 mL petroleum ether to (at maximum) 100 mg of sample. Subsequently, the mixture was centrifuged at 1600 rpm for 10 min. The supernatant solution containing maltenes was collected and the solvent removed through evaporation in a nitrogen atmosphere at 35 °C. Asphaltenes were then removed. The residual maltenes (up to 100 mg) were separated into aliphatic and aromatic fractions on silica gel (activated at 240 °C for 12 h), using a sequence of organic solvents of different polarity (petroleum ether, toluene).

Aliquots (1 μL) of each fraction were analysed by gas chromatography (GC) using an Agilent 7890A instrument, fitted with an on-column injector and an Agilent DB-5MS fused silica capillary column (60 m × 0.25 mm; df = 0.10 μm) coated with 95 % dimethylarylene siloxane and 5 % phenyl phase. Detection was achieved with flame ionization, with helium as the carrier gas. The temperature programme consisted of four stages: 80 °C held for 1 min; 80°-120 °C at 20 °C min^{-1}; 120°-300 °C at 3 °C min^{-1}; and 300 °C with the temperature held

for 35 min. GC-mass spectrometry (MS) analyses were performed using an Agilent 5975C mass selective detector (MSD) using the same column and temperature programme as for GC analyses. The MS operated with an ion-source temperature at 230 °C, electron ionization at 70 eV, and a cycle time of 1 sec in the mass range from 45 to 600 Da. In the selected ion mode (SIM) the dwell time of the operated MSD was set at 30 ms for each ion. Measurements of aliphatic fractions were carried out on a Thermo Scientific TSQ Quantum using parent-daughter-scans via multiple-reaction-monitoring (MRM), which overcomes most of the interference caused by co-eluting peaks. The instrument was tuned to a resolution of 0.7 mass units. The collision energy was 15 V with argon as the collision gas at a pressure of 1.0 mTorr. The column used was a 60-m CP-Sil-5 CB-MS with an i.d. of 0.25 mm and a film thickness 0.25 μm. The temperature programme was 50 °C held for 1 min; 50°-225 °C at 2 °C min^{-1}; 225°-300 °C at 20 °C min^{-1}; and 320 °C with the temperature held for 20 min.

Compounds were identified by comparison of retention times and mass spectra to the literature. Peak ratio calculations for GC-FID and GC-MS were done from integrated area:area and the biomarker ratios were computed as area:area as well. Individual compounds were identified and quantified relative to internal standards (ortho-terphenyl).

3.5. Stable carbon isotope analyses

Stable carbon isotope ratios of the C_{15+} saturated and aromatic hydrocarbon fractions were determined using a Finnigan Delta Plus MS. The $\delta^{13}C$ values are reported relative to the Vienna Pee Dee Belemnite (VPDB) standard, and the analytical error, determined by using co-injected standards, is ±0.2‰.

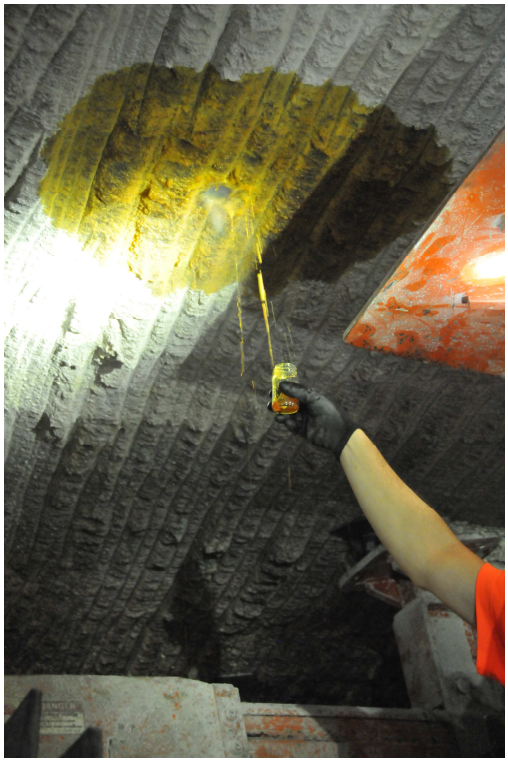


Fig. 4. Light-brown oil dripping out from fractures in rock salt of the Boulby Halite Formation from the roof of the Boulby Mine at a depth of 1100 m (mine working 2000 West Salt).

4. Structural geology and organic geochemistry

4.1. Seeping oil density

Oil samples can be classified as light oils with API gravity ranging from 35.1° to 42.2° (density 0.80984-0.84487 g/cm^3, Table 2), respectively, and cannot be linked directly to any particular oil in the North Sea such as Chalk Group-, KCF-, Zechstein-, Carboniferous- or Devonian-sourced oil (Evans et al., 2003).

4.2. Thermal maturity

Thermal maturity of Boulby oil and Malton 4 KAF samples (Table 1) is evaluated based on the saturated and aromatic hydrocarbon ratios listed in Table 1. These ratios may be affected by factors such as lithology and adsorption of OM on mineral surfaces, which may affect maturation signatures and variations in biomarker distributions (Jiang et al., 1988; Peters et al., 2005); thus interpretations should be based on a variety of maturity parameters.

The isoprenoid-based ratios Pr/*n*-C_{17} and Ph/*n*-C_{18} decrease with increasing thermal stress due to the preferential release of *n*-alkanes during maturation, but they can be affected by organofacies variation and biodegradation (Peters et al., 2005). These ratios show values

of 0.27 – 0.54 and 0.53–0.78 for Boulby oil samples and 0.17 – 0.58 and 0.21 – 0.58 for KAF samples, respectively (Table 3a, Fig. 5).

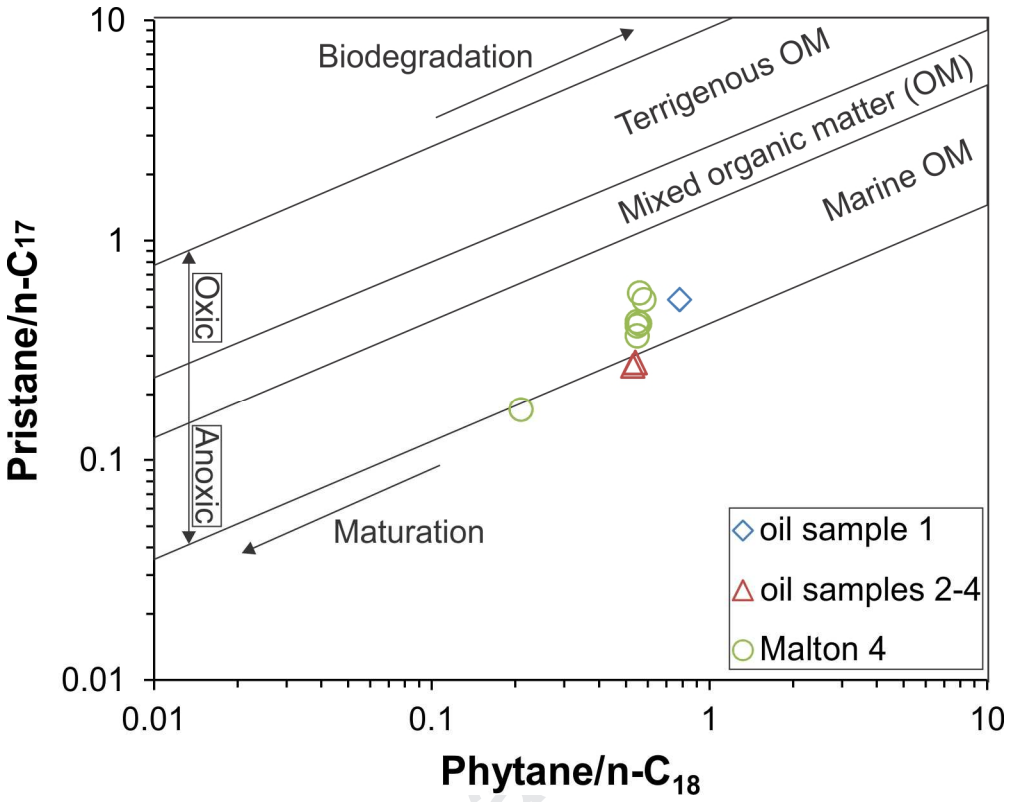


Fig. 5. Phytane to *n*-C_{18} alkane versus pristane to *n*-C_{17} alkane for Boulby oil (samples 1-4) and Malton 4 KAF samples (graphical fields after Shanmugam, 1985).

The Ts/Tm ratio calculated from oil sample 1 is 0.41 and 0.52 – 0.71 from Malton 4 KAF samples (Table 1). The Ts/Tm ratio can also be affected by lithology; for example, in carbonate settings Tm is preferentially generated (Peters et al., 2005). The M/H ratio in oil sample 1 is 0.12 and in KAF samples is 0.03 – 0.13 (Table 1). The M/H ratio decreases with thermal maturity from ~0.8 in immature bitumen to <0.15 in a mature source rock and oil to a minimum of 0.05 (Mackenzie et al., 1980; Seifert and Moldowan, 1980). In Boulby oil samples 2-4 the Ts/Tm and M/H ratios could not be determined due to high thermal maturity or OM alteration after deposition.

The isomerisation equilibrium for ββ/(αα + ββ) and 20S/(20S + 20R) C_{29} steranes lies between 0.67 – 0.71 and 0.52–0.57, respectively, and reaches equilibrium in the late and peak oil window, respectively (Peters et al., 2005). Therefore, C_{29} steranes may have a limited relevance in thermal maturity assessment (Walters et al., 2012). In oil sample 1 and KAF samples, values for the ββ/(αα + ββ) ratio are 0.56 and 0.45 – 0.58, respectively, whereas the

20S/(20S + 20R) values are 0.52 in oil sample 1 and 0.46 – 0.57 in KAF samples, indicating generation in the peak oil window (Table 1). The TA[I]/TA[I + II] ratio (Mackenzie et al., 1981) increases with increasing maturity (Beach et al., 1989) and is indicative of mature and late mature stages of oil generation (Peters et al., 2005). Values for TA[I]/TA[I + II] are 0.07 in oil sample 1 and 0.25 – 0.33 in KAF samples referring to the peak oil phase (Table 1). Values for regular sterane and triaromatic steroid ratios in oil samples 2-4 could not be determined due to the high thermal maturity of OM. As an alternative, a significant reduction in the distribution of terpenoids would not only result from high thermal maturity or diagenetic processes altering OM but also from the loss of more volatile hydrocarbons due to evaporation during the dripping out from fractures.

The MDR value is 4.88 in oil sample 1 and 1.78 – 2.02 in KAF samples, respectively, giving maturities in the range of 0.64 – 0.87 %Rm, whereas MPI 1 values in oil sample 1 (0.65) and oil samples 2-4 (1.3-1.4) give maturities in the range of 0.8-1.2 %Rc (Table 1) and in KAF samples (0.68 – 0.77) are 0.8-0.9 %Rc (Table 1), indicating peak oil window generation for oil sample 1 and KAF samples and late oil window generation for oil samples 2-4.

In summary, our data indicate that the Boulby oil samples were generated in the peak to late oil window and Malton 4 KAF samples in the peak oil window.

4.3. Molecular indicators of depositional environment

4.3.1. Stable carbon isotopes

The carbon isotopic compositions of aliphatic and aromatic hydrocarbons of crude oils are frequently used for correlation of oils (Fuex, 1977; Peters et al., 2005), to decipher their marine or terrigenous origin (Sofer, 1984; Chung et al., 1992), or age (Andrusevich et al., 1998). $\delta^{13}C$ values of the saturated fraction of the Boulby oil samples vary between -25.2 and -23.9 ‰, whereas the aromatic fraction has $\delta^{13}C$ values ranging from -24.4 to -22.6 ‰ (Fig. 6, Table 2). The canonical variable (CV, Sofer, 1984), which separates non-waxy (marine) and waxy (non-marine) oil, varies between -3 and -0.5 (Table 2). All signatures indicate that the source rock for the Boulby oil was deposited in a marine setting.

$\delta^{13}C$ values of the saturated and aromatic fractions of the Boulby oil are within the range of Late Permian (Zechstein) oil in Europe (i.e. -31 to -24‰), although the values between > -27.5 and -31‰ reported by Słowakiewicz et al. (2018) are of oils likely to have been generated from a different source rock than the Zechstein (unpublished data). The

Boulby $\delta^{13}C$ values are different from those of the Late Jurassic (-31.5 to -27.8‰; Bailey et al., 1990; Andrusevich et al., 2000; Peters et al., 2005; and this study) and Devonian (-35 to -31‰; Bailey et al., 1990; Peters et al., 2005) oil in the North Sea (Fig. 6).

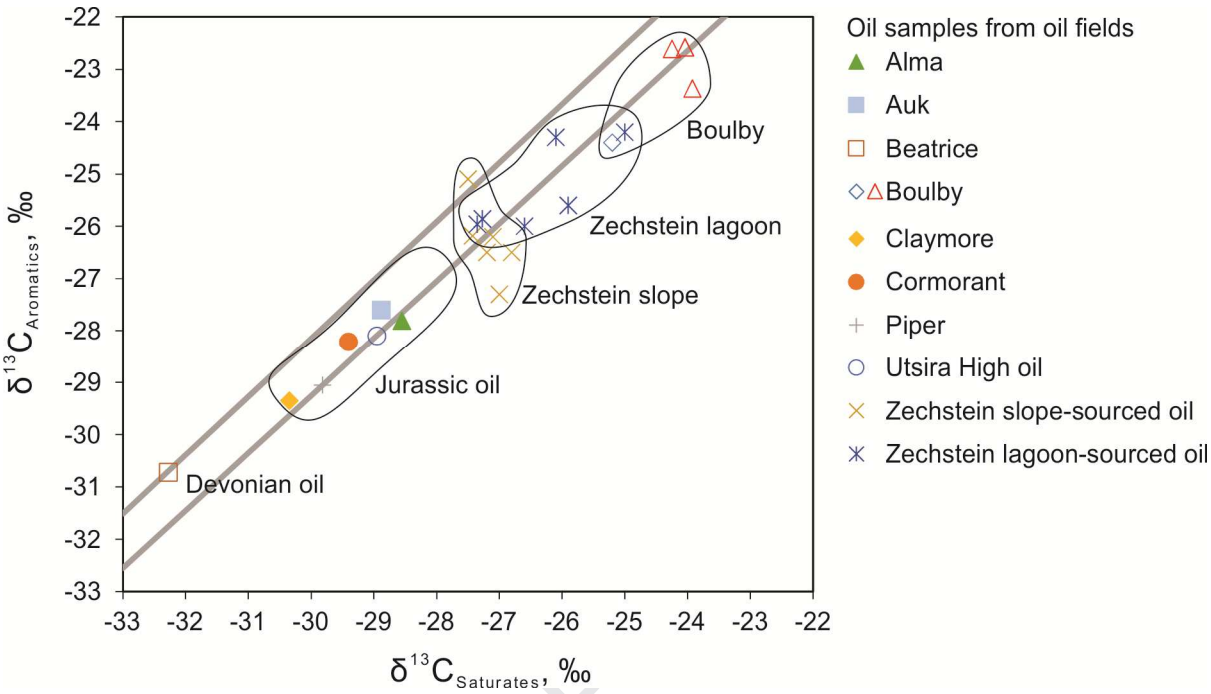


Fig. 6. Sofer's (1984) plot of $\delta^{13}C$ values for the saturated and aromatic fractions of various oil samples to compare with the Boulby oil. Late Jurassic (Alma, Auk, Claymore, Cormorant, Piper, from Peters et al., 2005 and this study + Utsira High oil + data from Bailey et al., 1990), Zechstein (from Słowakiewicz et al., 2018), and Devonian (Beatrice, from Peters et al., 2005) oils are given for comparison. Note that $\delta^{13}C$ values of Devonian oil shows and bitumen range from -31.4 to -35‰ (see Bailey et al., 1990).

4.3.2. Water column characteristics

A suite of biomarkers was used to assess redox conditions and depositional environment during formation of the source rocks for the Boulby oil, including the carbon preference index (CPI), Pr/*n*-C_{17} versus Ph/*n*-C_{18}, even-over-odd predominance (EOP) of *n*-alkanes, C_{31}-C_{35} homohopane distributions, and the homohopane index (HHI) expressed as C_{35}/(C_{31}-C_{35}) and $C_{35}S/C_{34}S$ (Table 3a-c). Triterpenoids in Boulby oil samples 2-4 were absent or significantly reduced due to high thermal maturity or OM degradation.

The CPI for all oil and KAF dolomite samples is close to 1 and 0.8 – 1, respectively, and an EOP for the C_{20-25} *n*-alkanes is observed in oil samples (Fig. 7). An EOP in the range of >*n*-C_{22} is typical of biomass deposited in restricted marine carbonate/evaporite facies (Dembicki et al., 1976; Shen et al., 1980; Palacas et al., 1984; Ten Haven et al., 1985) and

478 can also be attributed to some specific bacteria or fungi (Han and Calvin, 1969; Jones, 1969;
479 Fisher et al., 1972).

480 The values of Pr/*n*-C_{17} versus Ph/*n*-C_{18} in Figure 5 indicate primary accumulation of
481 marine OM under reducing conditions (Connan and Cassou, 1980; Palacas et al., 1984) for
482 the source rock of the Boulby oil. It should also be noted that short and long molecular
483 weight *n*-alkanes are reduced in some samples due to biodegradation (from non- to slight to
484 moderate biodegradation and presence of an unresolved complex mixture illustrated in Figure
485 7), thermal maturity (cracking), water washing or evaporative fractionation (Thompson, 1987,
486 1983; Holba et al., 1996; Akinlua et al., 2006). Homohopane distributions (Fig. 8) are used to
487 differentiate between oxic and reducing depositional environments, but the distributions can
488 be affected by thermal maturity and secondary alteration (Peters and Moldowan, 1991).
489 Slightly reducing (suboxic) depositional conditions are indicated by the HHI (0.14) and
490 $C_{35}S/C_{34}S$ ratio (0.8) for Boulby oil. Slightly more anoxic depositional conditions are
491 deduced for the KAF dolomite samples (Table 3b).
492
493

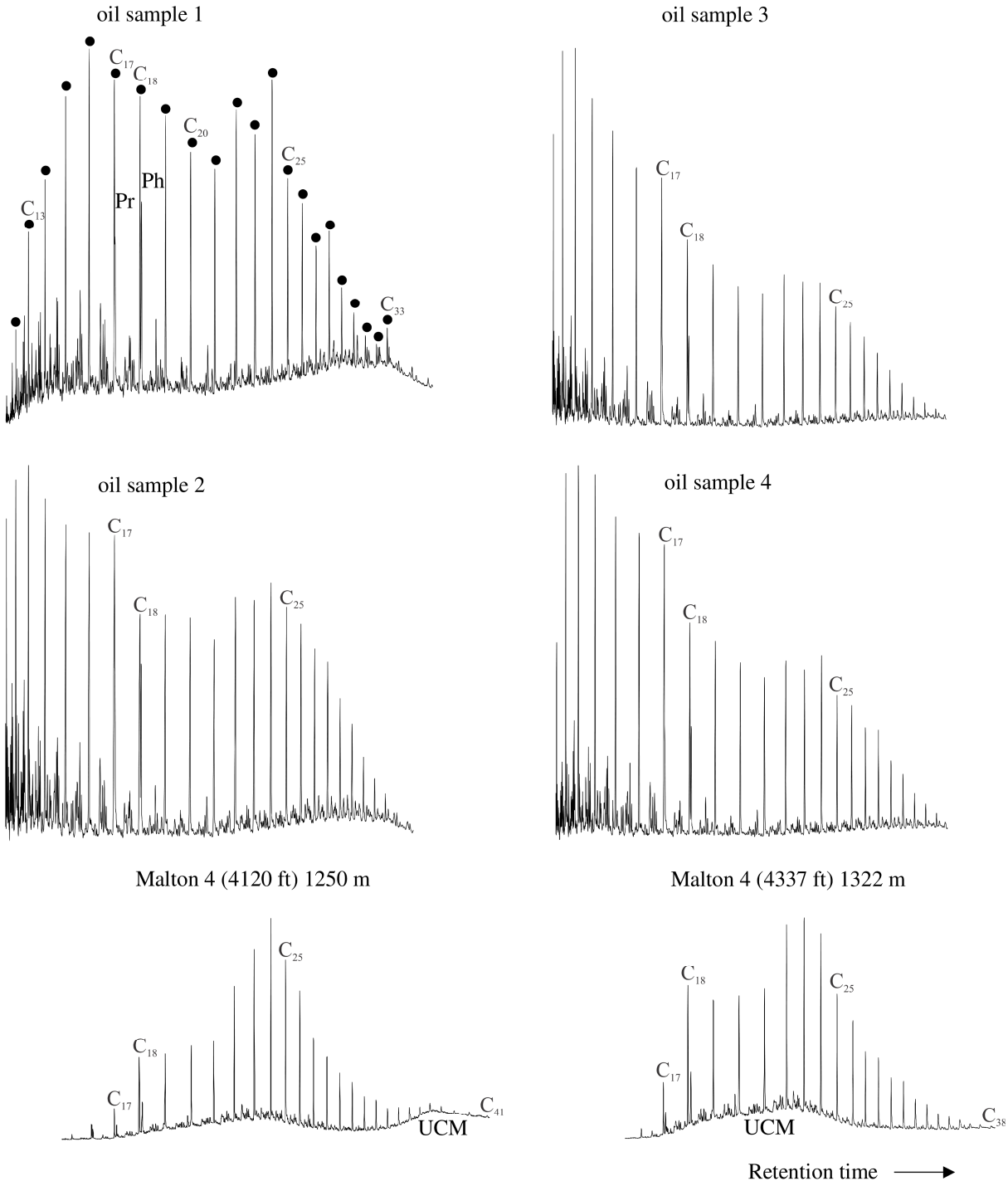


Fig. 7. Total ion current chromatograms of whole oil (Boulby oil samples 1 to 4) and selected Malton 4 dolomite (lagoonal facies) samples. Pr – pristane, Ph – phytane; black dots indicate *n*-alkanes. Note slight even-over-odd preference (EOP) for the C_{20-25} *n*-alkanes in Boulby oil samples. The EOP is not clear in Boulby oil sample 3. Note moderate biodegradation (classification after Wenger et al., 2002) with visible unresolved complex mixture (UCM for Malton 4 samples).

Boulby oil (particularly in oil sample 1) and KAF dolomite samples are characterized by the dominance of C_{30} 17αβ-hopane over lower or higher homologues and elevated relative

abundances of C_{32} and C_{34} hopanes (Boulby) and C_{32} and C_{35} hopanes (KAF) (Fig. 8, Table 3b), which are believed to indicate suboxic (high C_{32})/anoxic (high C_{34} or C_{35}) source-rock depositional environments (Peters and Moldowan, 1991). The dominance of 17αβ-C_{32} over C_{31} and C_{33} homologues and 17αβ-C_{34} over C_{33} and C_{35} homologues (Table 3b) indicates a carbonate lagoonal and evaporitic environment source (Palacas et al., 1984; Jiamo et al., 1986; Brassell et al., 1988; Waples and Machihara, 1991) or a depositional setting for oil shale (Kara-Gülbay and Korkmaz, 2008). However, elevated 17αβ-C_{34} and C_{35} hopanes are also characteristic for Late Permian (Zechstein) oil from south-central Germany derived from a carbonate-evaporite source rock (Słowakiewicz et al., 2018).

Biomarkers for anaerobic phototrophic green sulphur bacteria provide strong evidence of the redox state and water column stratification indicating photic zone euxinia (PZE) during source rock deposition (Summons and Powell, 1986; Sinninghe Damsté et al., 1993). Isorenieratene derivatives $C_{18\text{-}21}$ 2,3,6-aryl isoprenoids are present in oil sample 1 and KAF samples; in two KAF samples even isorenieratane has been detected (not shown). The absence or low abundance of isorenieratene derivatives in the other oil samples is likely a result of the thermal maturity effect (Requejo et al., 1992).

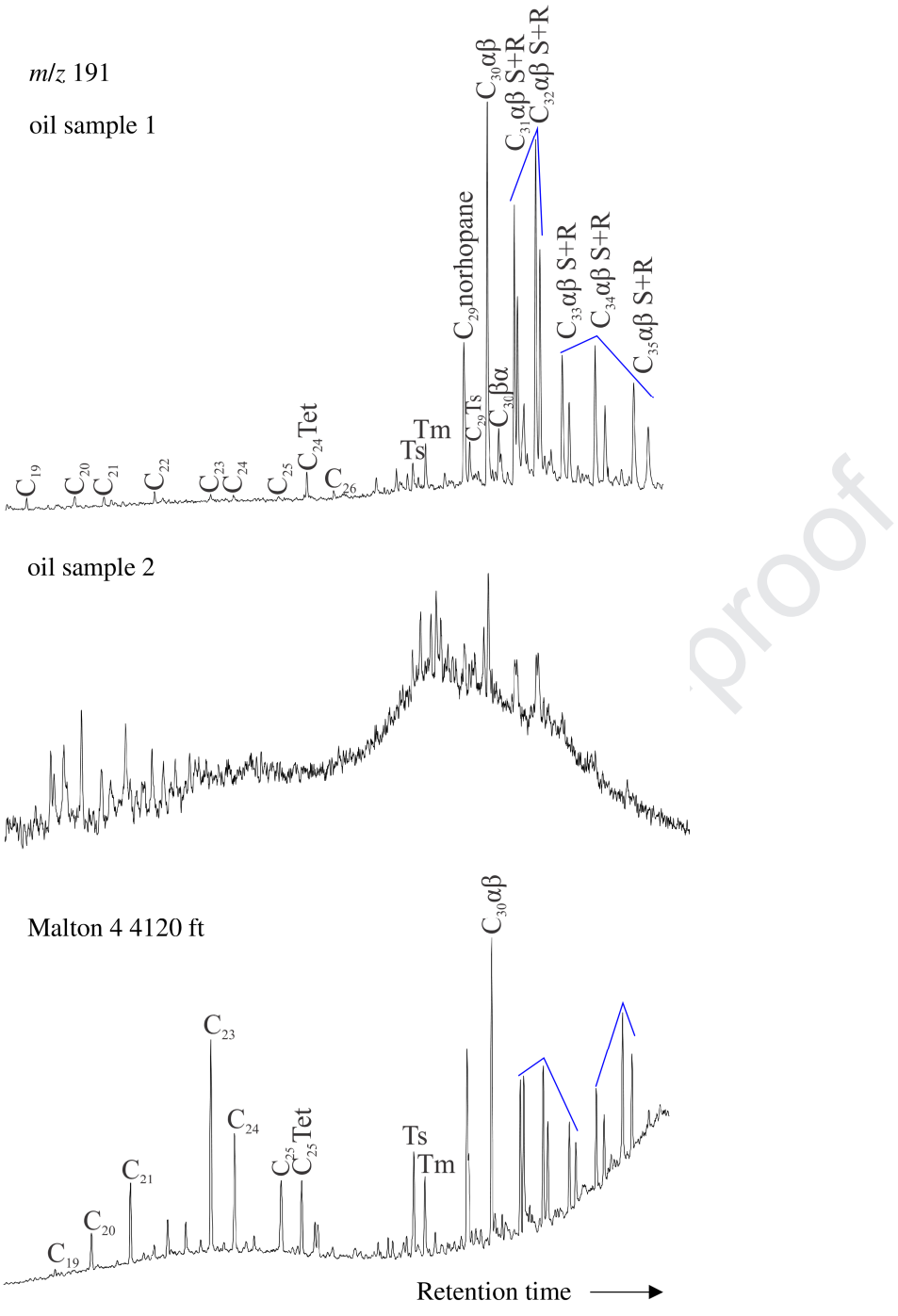


Fig. 8. Terpane mass chromatograms for Boulby oil samples and Malton 4 lagoonal facies have elevated C_{32}, C_{34} and C_{35} homohopanes indicating carbonate-evaporite source-rock depositional conditions. Some terpanes are absent in Boulby oil sample 2 due to high thermal maturity. Distribution of biomarkers in oil sample 2 is similar in oil samples 3 and 4.

4.3.3. Source of organic matter

The source rock for Boulby oil can be explored using $C_{35}S/C_{34}S$, the C_{29} 17αβ-norhopane/C_{30} 17αβ-hopane (C_{29}/H), C_{19}/C_{23} tricyclic terpane and diasterane/sterane ratios expressed as C_{27} or C_{29} 13β,17α(H) (20S + 20R)/(C_{27} or $_{29}$ 5α,14α,17α(H) 20S + 20R + 5α,14β,17β(H) 20S + 20R).

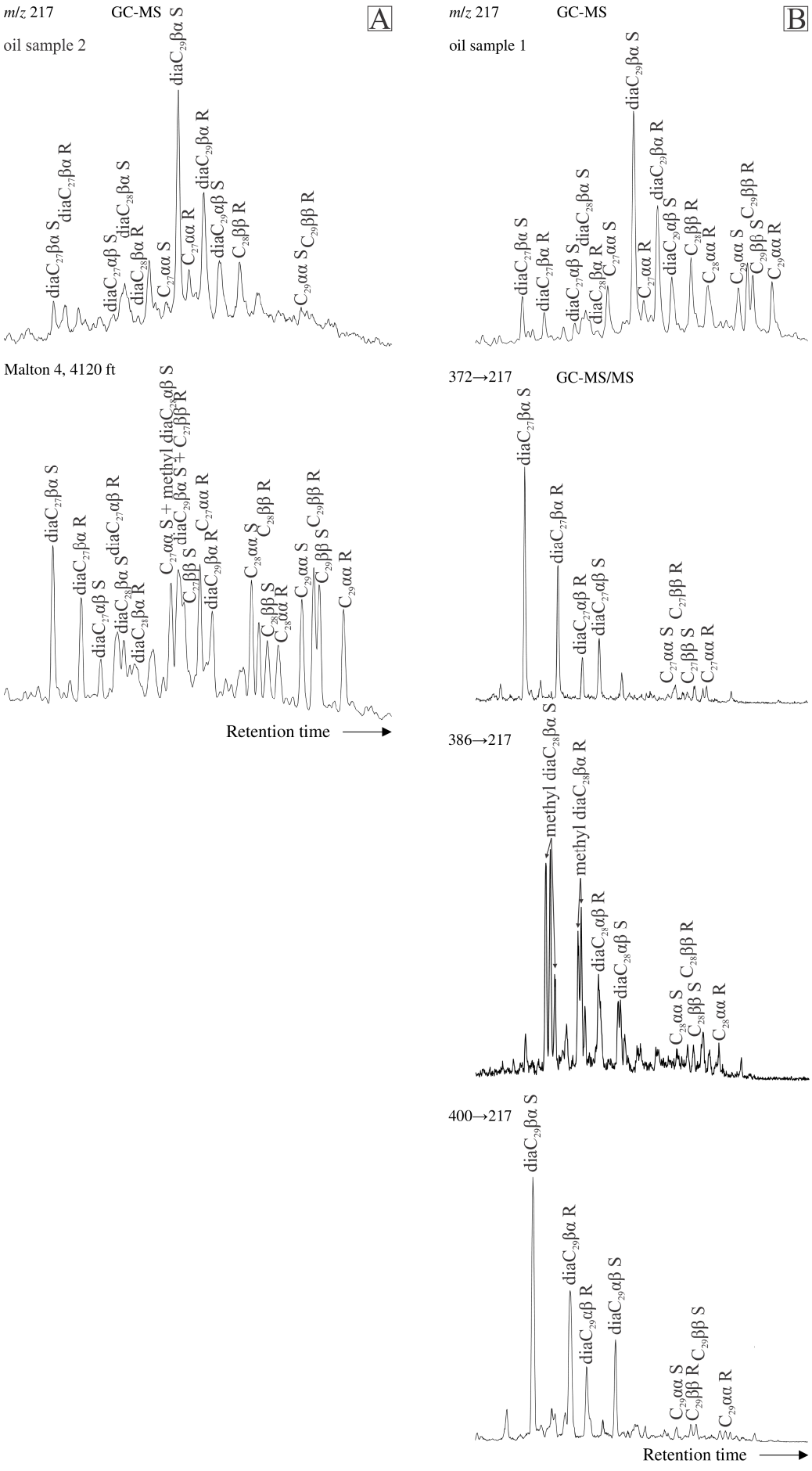
High C_{29}/H (>0.8) in oil is commonly reported as derived from anoxic carbonate or a marl source rock (Palacas et al., 1984; Clark and Philp, 1989). In oil sample 1 the C_{29}/H ratio is 0.27 and in KAF dolomite samples this ranges from 0.5 to 1.2 (mean 0.74) (Table 3a) and, in tandem with $C_{35}S/C_{34}S$, suggests a clay-rich source rock (Peters et al., 2005).

The C_{19}/C_{23} tricyclic terpane ratio is used to distinguish between algal/microbial and terrigenous sources of OM because C_{19} is mainly derived from higher plants, whereas C_{23} is a predominant component of algal and microbial OM (Simoneit, 1977). High values of the ratio indicate oils derived from source rocks containing significant amounts of terrigenous OM, whereas oils originating from algal/microbial OM have low values. All samples (Boulby oils and Malton 4 dolomites) have low values (0.03 – 0.24; Table 3a) of the C_{19}/C_{23} ratio suggesting that OM is dominated by marine algal/microbial components.

The diasterane/sterane ratio also helps to distinguish oil from carbonate versus clastic source rock (Mello et al., 1988). High diasterane/sterane ratios are typically interpreted to be derived from a clay-rich source rock but high ratios have also been observed in extracts from organic-lean and clay-poor carbonate rock (Palacas et al., 1984; Moldowan et al., 1991), or they might result from high thermal maturity or heavy biodegradation (Seifert and Moldowan, 1978, 1979), also in the case of coals (Killops et al., 1994). The diasterane/sterane ratio (C_{27} and C_{29}) in all oil samples of between 0.3 and 0.9 and in KAF dolomite samples (0.3 – 4) suggests a carbonate-evaporite source rock with an abundant clay (marl) content (Table 3b). Importantly, a very characteristic biomarker for all Boulby oil samples is an unusually abundant C_{29} 24-ethyl-13β(H),17α(H)-diacholestane (20S) (Fig. 9). High abundances of C_{29} diasteranes (20S + 20R) have also been found in the Middle Jurassic Sanjianfang Formation oil generated from the Xishanyao Formation coal interbedded with shale (Sun et al., 2000). Therefore, given the high diasterane/sterane ratio in Boulby oil samples (Table 3b), we tentatively assign C_{29} 24-ethyl-13β(H),17α(H)-diacholestane (20S) to the clay source.

In summary, Boulby oil was generated from a source rock deposited under suboxic-anoxic marine carbonate-evaporite-clayey conditions similar to the depositional conditions of KAF lagoonal facies. The absence of 28,30-bisnorhopane (BNH) commonly found in KCF kerogen and oil in the North Sea (Grantham et al., 1980) argues against an Upper Jurassic

source rock for Boulby oil, although this should be treated with caution because BNH decreases with increasing thermal maturity (Peters et al., 2005). However, the BNH/17αβ-C_{30} ratio (0.01-0.06) applied as a facies parameter is typical of Zechstein Main Dolomite oil in other parts of the SPB (Petersen et al., 2016; Słowakiewicz, 2016; Słowakiewicz et al., 2018), although BNH was not detected in KAF dolomite samples either. Gammacerane, commonly invoked as evidence for a stratified water column in marine and non-marine depositional environments and/or specifically for hypersalinity (Moldowan et al., 1985; Jiamo et al., 1986; Sinninghe Damsté et al., 1995), is also absent. This suggests that OM may not have been deposited under high-salinity conditions or gammacerane has not been preserved. The predominance of 17αβ-C_{34} or C_{35} homologues has been found to be characteristic of Zechstein oil (Słowakiewicz et al., 2018), and dominance of 17αβ-C_{32} and C_{35} homologues occurs in Malton 4 KAF lagoonal carbonate rocks (Słowakiewicz et al., 2016, and this study).


m/z 217
GC-MS
A
oil sample 2
diaC27βα S
diaC27βα R
diaC27αβ S
diaC28βα S
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Retention time
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GC-MS
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oil sample 1
diaC27βα S
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Retention time

Fig. 9. Sterane mass chromatograms (GC-MS and GC-MS/MS) for Boulby oil and Malton 4 KAF samples. (A) Boulby oil sample 2 and Malton 4 lagoonal facies sample are given for comparison; (B) Note that Boulby oil samples have elevated C_{29} 24-ethyl-13β(H),17α(H)-diacholestane (20S) tentatively assigned to high abundance of clay-rich organic matter.

4.3.4. 3D seismic and fluid migration

Interpretation of the seismic data cube resulted in the definition of three main structural trends (Figs. 10, 11).

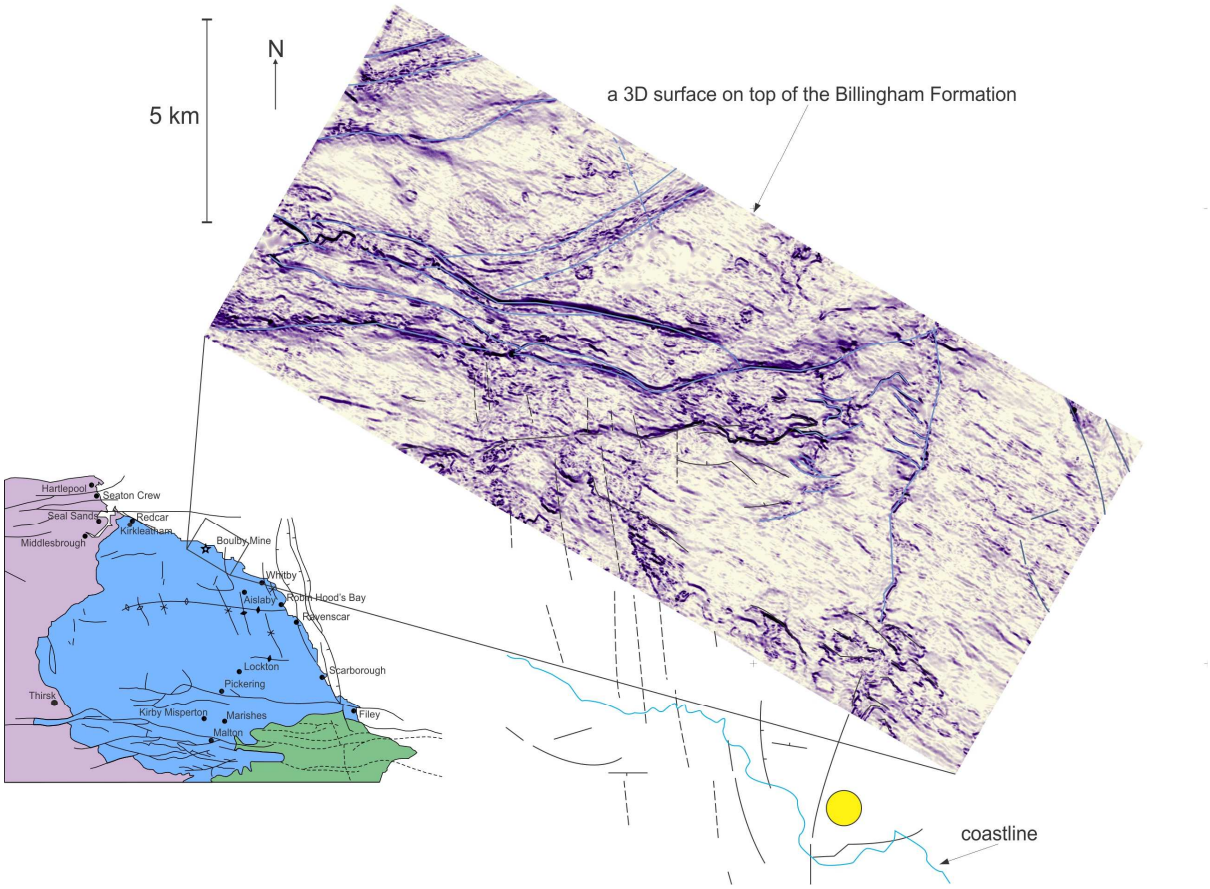


Fig. 10. Dip map highlighting the regional context and variation in dips. The darker areas of strong dip highlight major structures affecting the top of the Billingham Formation anhydrite (EZ3A). Sampling location is marked by the yellow circle.

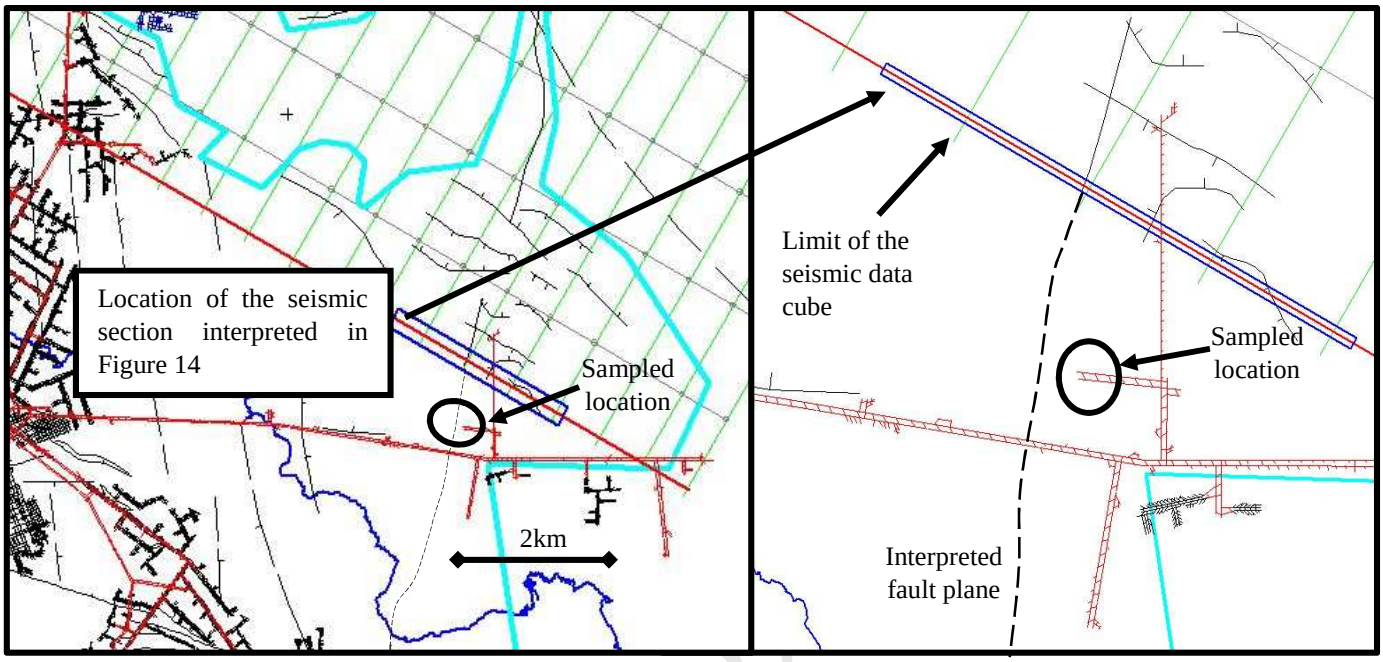


Fig. 11. Map of the Boulby oil sampling location and its relation to the seismic survey area (inset). Major structural features are highlighted (courtesy of ICL UK). Light blue line is the 'seismically quiet' area identified by the 3D survey.

1) East-west trending faults which cut across the offshore area in the centre of the data cube: There is an indication of separation along these faults between shallower and deeper sections where plastic flow of the halite, marl and potash intervals within the upper part of the EZ3 and lower EZ4 cycles accommodates brittle displacement in the underlying sequence (Fig. 10, Hardy, 2011 unpublished).

2) Northeast-southwest faults (Fig. 12): This system is composed of deep level *en-echelon* and shallow through-going components. There are complex interactions with the east-west faulting and seismic data indicate extensive thinning and possible absence of halite/potash at the junction of the two fault systems.

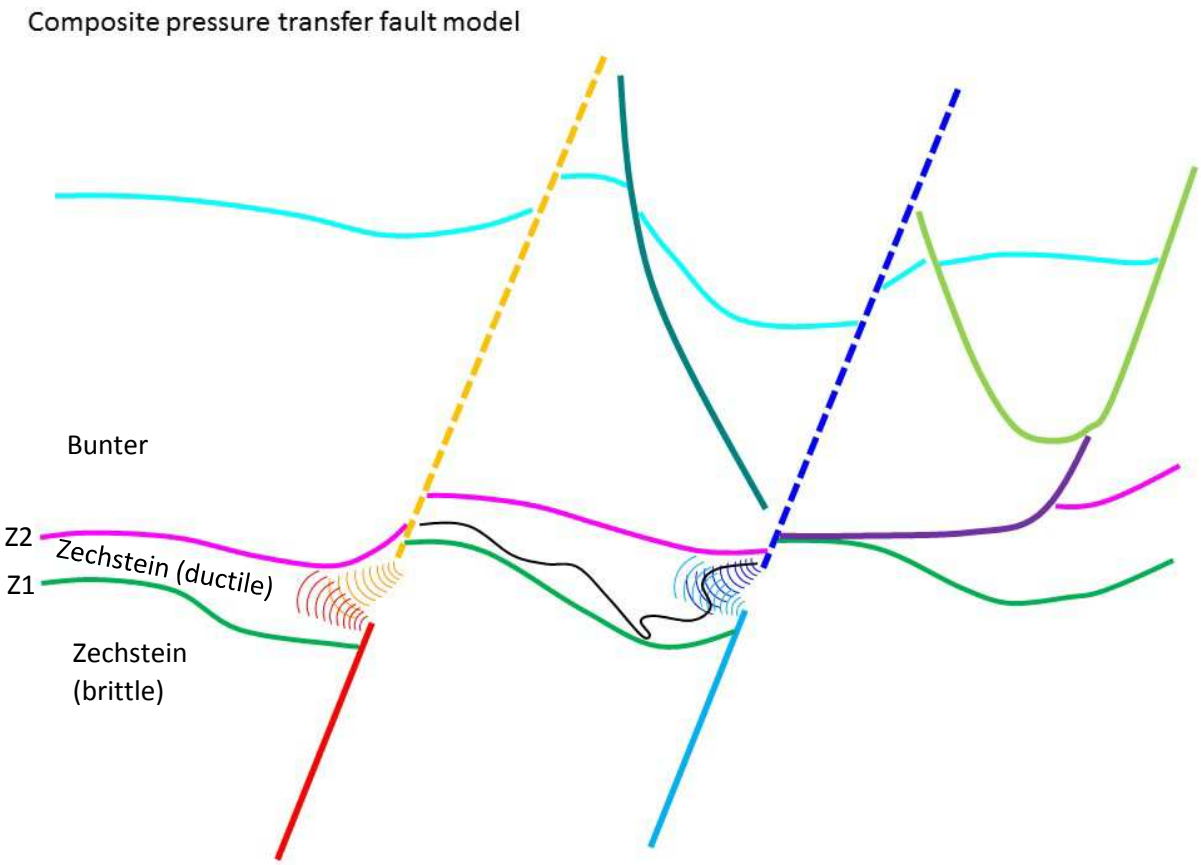


Fig. 12. Current cross-section model of the faults affecting the various strata within the study area, highlighting the observed dissipation of fault offset by plastic strata in the two Zechstein horizons (Z1 + Z2) as well as the brittle fracturing in anhydrite and dolomite below (Hardy, 2011 unpublished). Model has planar (or near planar) faulting above and below which effectively terminates on entering the plastic, mobile Zechstein rock. The energy of the fault movement dissipates as a pressure front through the rock causing flow in the mobile units (i.e., potash, marls) and fracturing in the interstitial brittle units (i.e., dolomite) (courtesy of Israel Chemicals Ltd).

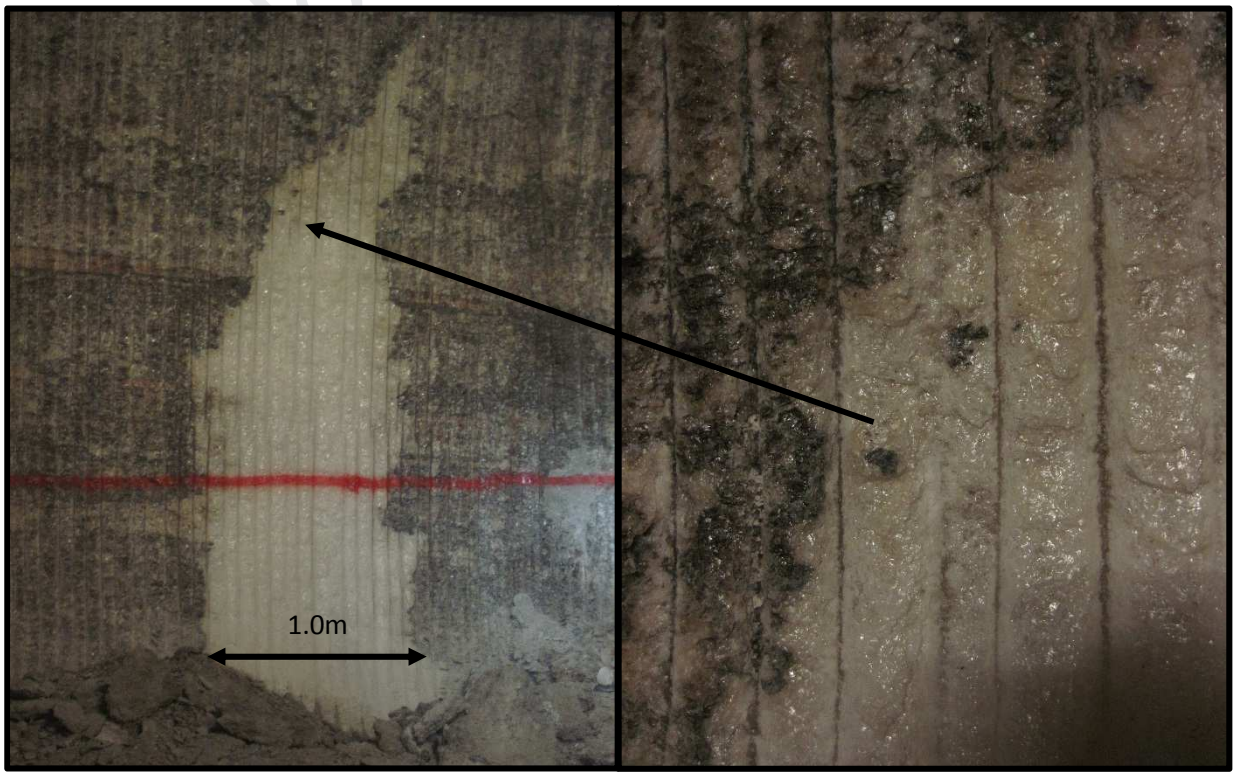
3) North-south faults: These form part of the Peak Fault system (Milsom and Rawson, 1989) and are the most relevant trend for this study. These N-S faults are known to have been active during Jurassic times, i.e., they show evidence for synsedimentary movements. Other synsedimentary N-S faults in the Cleveland Basin include the Whitby Harbour Fault and the Runswick Bay Fault, relatively close to the Boulby Mine. The N-S fault structure interacts directly with the area from which the oil described herein and that previously encountered by mining were collected. Although direct intersection of the fault plane by drilling is limited, significant occurrences of thinned/absent strata, washouts, collapse breccias and evidence for geologically high fluid flux are common throughout the region surrounding this system over

many kilometres. These features indicate that the Peak Fault system has acted as a fluid pathway for brine and oil, presumably sourced from depth and localised within the Boulby Halite Formation.

Numerous H_2S and hydrocarbon-rich halite horizons and seeps from anhydrite were detected whilst crossing this area with exploratory wells. All workings mined across the fault were subject to ingress of light oil and gas not normally encountered elsewhere in the mine, the majority of which appear to be trapped at or below the Boulby Potash Member (EZ3K) level.

Further evidence of the upward migration of fluids within the EZ3 halite was demonstrated when mining revealed a series of pillar-like bodies of white coarse-grained halite within the normal laminar halite strata (EZ3Na); these structures demonstrate cross-cutting relationships to the EZ3 halite and fragments of the surrounding rock could be seen breaking off at the tip of the structure (Fig. 13).

Adjacent seismic sections (Fig. 14) illustrate this zone of faulting and disturbance. Breaks in a number of stratigraphic markers, in particular the Billingham Formation anhydrite, can be picked out and a zone of ductile deformation which can be seen extending ~100-200 m away from the fault.



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673 **Fig. 13.** Two photographs illustrating a cross-cutting white halite pillar with associated hydrocarbon residue
674 trapped towards the tip within the EZ3Na halite, Boulby Mine. Approximate field of view: 3.5m H x 2.0m W
675 (photograph courtesy of Israel Chemicals Ltd).

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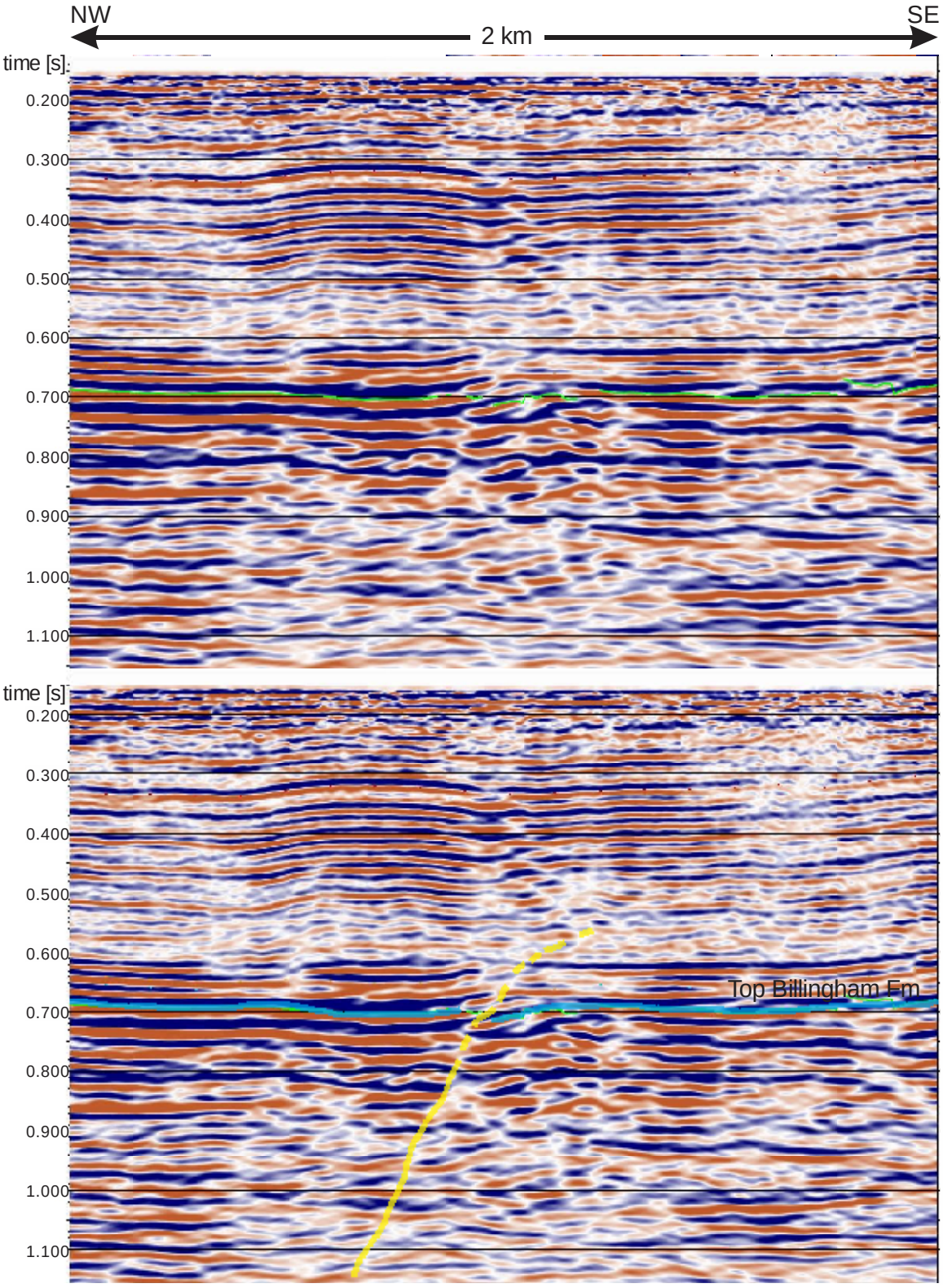

677

678 **Fig. 14.** Clean and interpreted seismic section pair through the fault zone adjacent to the sampling location. Top
679 of the Billingham Formation anhydrite marked approximately half-way down the section with the fault picked
680 out in yellow. Vertical scale: time in seconds (sections courtesy of Israel Chemicals Ltd).

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5. Discussion

From time to time oil is encountered during mining operations at Boulby Potash Mine on the coast of Yorkshire. 'Live' flowing oil was encountered in early September 2018 and sampled immediately. The analytical results of biomarker distributions demonstrate clearly that Boulby oil was generated locally from three likely source rocks: the Brotherton Formation (EZ3Ca = Plattendolomit), the KAF (EZ2Ca = Hauptdolomit) and Namurian oil shale, although, as noted earlier, one other possibility is OM from microbialites within anhydrite facies, i.e., Hayton (EZ1A), Fordon (EZ2A) and Billingham (EZ3A) anhydrites. The Brotherton Formation (26 m thick) consists of very dark grey to black fine-grained muddy carbonate, mostly dolomite, and locally this rock contains dolopackstone formed by the green alga *Calcinema*. The Brotherton is located some 50 m below the mine working where the oil was collected, and it has been encountered in drilling for polyhalite (Z2 age) which occurs just below that carbonate. The KAF carbonate is present 200 m below the halite from which the oil drips, and here it is likely to be in a mid-outer ramp facies with a thickness in the region of approximately 200 m, although the actual thickness has not been established. This KAF facies has been examined from two boreholes in North Yorkshire, 30 km (Lockton) and 50 km (Malton) south of the Boulby Mine (Fig. 1; Słowakiewicz et al., 2016, and this study). Here, OM from Lockton KAF lower slope facies has high thermal maturity (reduced or absent hopanes and steranes), likely resulting from burial diagenetic or hydrothermal influence, but OM from Malton KAF lagoonal facies is within the peak oil window for hydrocarbon generation. Distribution of *n*-alkanes in the latter is unimodal or bimodal and *n*-C_{18} and *n*-C_{23} or *n*-C_{24} are the most abundant unless samples are biodegraded or thermally altered. Gammacerane and BNH are absent; C_{32} and C_{35} homohopanes dominate over C_{31} and C_{33} or C_{34} homologues, respectively, and C_{27} and/or C_{29} regular steranes are predominant (Figs. 8,9). OM is clay-rich as also identified in Boulby oil samples. Hence, most likely the lagoonal dolomite identified in the KAF might be the source rock for Boulby oil. Such marly algal-microbial dolomite source rocks are well documented in Central Europe and they form an important source rock for oil in the German and Polish sections of the SPB (Słowakiewicz et al., 2018). However, never before has mature Zechstein oil been found so far west.

Zechstein evaporites, which seal KAF's stratigraphic equivalents elsewhere in the SPB, containing clay-rich chicken-wire anhydrite, have been interpreted as important contributors to a source rock for Zechstein oil (Słowakiewicz et al., 2018). Yet, biomarker distributions and their characteristics obtained from the Hartlepool Anhydrite (= Z1A, Werraanhydrit, 590-1020 ft [179.8-310.9 m]) from Durham Offshore Borehole No. 1 do not match those of Boulby oil; more data are needed to prove these rocks as a potential source rock for petroleum in the North Sea (our unpublished data).

The second significant source rock for Boulby oil could be Namurian (Edale Shale Group) oil shale. It was deposited in a distal pro-delta setting (Fraser et al., 1990) and hence the OM is of predominantly terrigenous type. However, the high abundance of diasteranes (particularly C_{29} diacholestane 20S) in the Boulby oil is more likely to be a reflection of a marine clay rather than a terrigenous OM source; it is noteworthy that the OM in the KAF dolomite samples is also of marine clay-rich type. Importantly, Namurian source rock in the Boulby area is in both the peak oil and gas window (Fraser et al., 1990; Heath-Clarke et al., 2016; Haarhoff et al., 2018); this is closely similar to the interpreted peak to late oil window for hydrocarbon generation of the Boulby oil. However, the oil residues filling fractures in the Devonian Weardale Granite in Co. Durham (100 km NW of Boulby), which were probably derived from a mid-Carboniferous source rock (Baba et al., 2019) have significantly different distributions of *n*-alkanes, steranes and hopanes compared to the Boulby oil and KAF dolomite samples. In addition, Edale Shale Group oil shale has not been identified in the close vicinity of the Boulby Mine and 41/18-1 mudrock samples. Finally, the structural pattern in the Boulby area and presence of several fault systems would have created excellent conduits for fluid migration from the Zechstein KAF source rock to more porous portions of Brotherton Formation dolomite. As reported by Holmes (1991) and presented herein, the presence of a reverse fault well exposed by mine workings (Fig. 13) results in a 35-m vertical displacement of the Brotherton Formation dolomite and Z3 evaporites (anhydrite, halite and potash beds) are draped over it. Boulby oil seeped from the Brotherton Formation carbonate rocks when they were first encountered during drilling at the mine (Davison, 2009) so that the oil must be migrating up from lower stratigraphic levels (KAF) into the Boulby Halite through some transient faults, although Z3 anhydrite and halite would mostly act as seals. The latter and, along with the underlying Roxby Formation marl, which is ~125 m thick in the Boulby Mine area, may have prevented the Boulby oil from reaching the porous Sherwood Sandstone Group strata above.

To date, the perceived primary exploration risk in the offshore area has been an absence of an oil source rock. The presence of thermally mature Zechstein source rock in this western UK sector of the North Sea is important because much of the recently offered exploration acreage in the UK 30th and 31st Licencing rounds is just ~50 km east of the proven oil at Boulby.

6. Conclusions

The investigated origin of the Boulby oil, seeping from fractures in the Boulby Halite Formation rock salt, and based on its stable carbon isotopes, biomarker distributions and structural pattern, is that it was likely derived from Zechstein 2 Kirkham Abbey Formation sapropelic dolomite and reservoired by Zechstein 3 Brotherton Formation dolomite. The thermal maturity of the analysed oil is in the peak to late oil window.

$\delta^{13}C$ values and biomarker signatures of saturated and aromatic hydrocarbon fractions show that oil samples were not derived from Devonian or Late Jurassic source rocks. With respect to source, a carbonate-evaporite depositional setting is indicated by the high abundance of C_{32} and C_{34} homohopane homologues and EOP of $C_{20\text{-}25}$ *n*-alkanes whereas clay-rich (but not terrigenous) OM is implied by the abundant C_{29} ethyl-diacholestane 20S, which seem to be characteristic biomarkers of the Boulby oil. The source rock was deposited under marine and suboxic-anoxic conditions. Similar biomarker distributions (apart from abundant C_{29} ethyl-diacholestane 20S) have been detected in Malton 4 KAF dolomite samples, suggested to be the likely source rock for the Boulby oil.

Collectively, biomarker fingerprints and seismic data have allowed the identification of depositional environment, OM source, thermal maturity and migration pathways of Boulby oil in the Cleveland Basin.

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Author contributions

M.S. designed the project, analysed the data and wrote the manuscript. This study is partly based on S.S.'s BSc thesis (Słama, 2019) supervised by M.S., which provided some biomarker analyses. J.G. provided oil samples. A.K. performed the GC-FID and GC-MS. T.E. and P.S. provided seismic and geological data and oil samples. J.G., S.S., M.M., M.E.T., I.P. contributed to writing the article. All authors approved the manuscript.

References

Akinlua, A., Ajayi, T.R., Adeleke, B.B., 2006. Niger Delta oil geochemistry: Insight from light hydrocarbons. Journal of Petroleum Science and Engineering 50, 308–314. https://doi.org/10.1016/j.petrol.2005.12.003

Andrews, I.J., 2013. The Carboniferous Bowland Shale gas study: geology and resource estimation. British Geological Survey for Department of Energy and Climate Change, London, UK.

Andrusevich, V.E., Engel, M.H., Zumberge, J.E., 2000. Effects of paleolatitude on the stable carbon isotope composition of crude oils. Geology 28, 847–850. https://doi.org/10.1130/0091-7613(2000)28<847:EOPOTS>2.0.CO;2

Andrusevich, V.E., Engel, M.H., Zumberge, J.E., Brothers, L.A., 1998. Secular, episodic changes in stable carbon isotope composition of crude oils. Chemical Geology 152, 59–72. https://doi.org/10.1016/S0009-2541(98)00096-5

Armstroff, A., 2004. Geochemical significance of biomarkers in Paleozoic coals, PhD dissertation. Berlin.

Baba, M., Parnell, J., Bowden, S., Armstrong, J., Perez, M., Wang, X., 2019. Emplacement of oil in the Devonian Weardale Granite of northern England. Proceedings of the Yorkshire Geological Society 62, 229–237. https://doi.org/10.1144/pygs2018-008

Bailey, N.J.L., Burwood, R., Harriman, G.E., 1990. Application of pyrolysate carbon isotope and biomarker technology to organofacies definition and oil correlation problems in North Sea basins. Organic Geochemistry 16, 1157–1172. https://doi.org/10.1016/0146-6380(90)90151-O

Barnard, P.C., Cooper, B.S., 1983. A review of geochemical data related to the Northwest European Gas Province. Geological Society, London, Special Publications 12, 19–33. https://doi.org/10.1144/GSL.SP.1983.012.01.04

Beach, F., Peakman, T.M., Abbott, G.D., Sleeman, R., Maxwell, J.R., 1989. Laboratory thermal alteration of triaromatic steroid hydrocarbons. Organic Geochemistry 14, 109–111. https://doi.org/10.1016/0146-6380(89)90024-7

816 Besly, B.M., 1998. Carboniferous, in: Glennie, K.W. (Ed.), Petroleum Geology of the North Sea.
817 Blackwell Science Ltd, pp. 104–136.
818 Brassell, S.C., Eglinton, G., Sheng, G., Fu, J., 1988. Biological markers in lacustrine Chinese oil shales.
819 Geological Society, London, Special Publications 40, 299–308.
820 https://doi.org/10.1144/GSL.SP.1988.040.01.24
821 Burgess, P.M., Gayer, R.A., 2000. Late Carboniferous tectonic subsidence in South Wales:
822 implications for Variscan basin evolution and tectonic history in SW Britain. Journal of the
823 Geological Society 157, 93–104. https://doi.org/10.1144/jgs.157.1.93
824 Chadwick, R.A., Holliday, D.W., Holloway, S., Hulbert, A.G., 1993. The evolution and hydrocarbon
825 potential of the Northumberland–Solway Basin. Geological Society, London, Petroleum
826 Geology Conference series 4, 717–726. https://doi.org/10.1144/0040717
827 Chung, H.M., Rooney, M.A., Toon, M.B., Claypool, G.E., 1992. Carbon isotope composition of marine
828 crude oils. AAPG Bulletin 76, 1000–1007.
829 Clark, J.P., Philp, R.P., 1989. Geochemical characterization of evaporite and carbonate depositional
830 environments and correlation of associated crude oils in the Black Creek Basin, Alberta.
831 Bulletin of Canadian Petroleum Geology 37, 401–416.
832 Connan, J., Cassou, A.M., 1980. Properties of gases and petroleum liquids derived from terrestrial
833 kerogen at various maturation levels. Geochimica et Cosmochimica Acta 44, 1–23.
834 https://doi.org/10.1016/0016-7037(80)90173-8
835 Cooper, B.S., Barnard, P.C., Telnaes, N., 1995. The Kimmeridge Clay Formation of the North Sea, in:
836 Katz, B.J. (Ed.), Petroleum Source Rocks. Springer Berlin Heidelberg, Berlin, Heidelberg, pp.
837 89–110. https://doi.org/10.1007/978-3-642-78911-3_6
838 Corfield, S.M., Gawthorpe, R.L., Gage, M., Fraser, A.J., Besly, B.M., 1996. Inversion tectonics of the
839 Variscan foreland of the British Isles. Journal of the Geological Society 153, 17–32.
840 https://doi.org/10.1144/gsjgs.153.1.0017
841 Craig, J., Gluyas, J., Laing, C., Schofield, P., 2015. Hardstoft – Britain's first oil field. Search and
842 Discovery Article #70188.
843 Creaney, S., Jones, J.M., Holliday, D.W., Robson, P., 1980. The occurrence of bitumen in the Great
844 Limestone around Matfen, Northumberland – its characterisation and possible genesis.
845 Proceedings of the Yorkshire Geological Society 43, 69–79.
846 https://doi.org/10.1144/pygs.43.1.69
847 Daniels, S.E., Tucker, M.E., Mawson, M.J., Holdsworth, R.E., Long, J.J., Gluyas, J.G., Jones, R.R., 2020.
848 Nature and origin of collapse breccias in the Zechstein of NE England: local observations with
849 cross-border petroleum exploration and production significance, across the North Sea.
850 Geological Society, London, Special Publications 494. https://doi.org/10.1144/SP494-2019-
851 140
852 Davison, I., 2009. Faulting and fluid flow through salt. Journal of the Geological Society 166, 205–216.
853 https://doi.org/10.1144/0016-76492008-064
854 de Leeuw, J.W., Sinninghe Damsté, J.S., 1990. Organic sulphur compounds and other biomarkers as
855 indicators of palaeosalinity, in: Orr, W.L., White, C.M. (Eds.), Geochemistry of Sulfur in Fossil
856 Fuels, ACS Symposium Series. American Chemical Society, pp. 417–443.
857 https://doi.org/10.1021/bk-1990-0429.ch024
858 DECC, 2013. The hydrocarbon prospectivity of Britain's onshore basins. Department of Energy &
859 Climate Change, 86p.
860 Dembicki, H., Meinschein, W.G., Hattin, D.E., 1976. Possible ecological and environmental
861 significance of the predominance of even-carbon number C20-C30n-alkanes. Geochimica et
862 Cosmochimica Acta 40, 203–208. https://doi.org/10.1016/0016-7037(76)90177-0
863 Duguid, C., Underhill, J.R., 2010. Geological controls on Upper Permian Plattendolomit Formation
864 reservoir prospectivity, Wissey Field, UK Southern North Sea. Petroleum Geoscience 16,
865 331–348. https://doi.org/10.1144/1354-0793/10-021

Evans, D., Graham, C., Armour, A., Bathurst, P. (Eds.), 2003. The millennium atlas: Petroleum geology of the Central & Northern North Sea. Geological Society of London.

Fisher, D.J., Holloway, P.J., Richmond, D.V., 1972. Fatty acid and hydrocarbon constituents of the surface and wall lipids of some fungal spores. Microbiology, 72, 71–78. https://doi.org/10.1099/00221287-72-1-71

Fraser, A.J., Gawthorpe, R.L., 1990. Tectono-stratigraphic development and hydrocarbon habitat of the Carboniferous in northern England. Geological Society, London, Special Publications 55, 49–86. https://doi.org/10.1144/GSL.SP.1990.055.01.03

Fraser, A.J., Nash, D.F., Steele, R.P., Ebdon, C.C., Fraser, A.J., 1990. A regional assessment of the intra-Carboniferous play of Northern England. Geological Society, London, Special Publications 50, 417–440. https://doi.org/10.1144/GSL.SP.1990.050.01.26

French, K.L., Sepúlveda, J., Trabucho-Alexandre, J., Gröcke, D.R., Summons, R.E., 2014. Organic geochemistry of the early Toarcian oceanic anoxic event in Hawsker Bottoms, Yorkshire, England. Earth and Planetary Science Letters 390, 116–127. https://doi.org/10.1016/j.epsl.2013.12.033

Fuex, A.N., 1977. The use of stable carbon isotopes in hydrocarbon exploration. Journal of Geochemical Exploration 7, 155–188. https://doi.org/10.1016/0375-6742(77)90080-2

Gautier, D.L., 2005. Kimmeridgian shales total petroleum system of the North Sea Graben Province. U.S. Geological Survey Bulletin 2204-C, 24p.

Glennie, K.W., Higham, J., Stemmerik, L., 2003. Permian, in: Evans, D., Graham, C., Armour, A., Bathurst, P. (Eds.), The Millenium Atlas: Petroleum Geology of the Central and Northern North Sea. Geological Society of London, London, pp. 91–103.

Glennie, K.W., Underhill, J.R., 1998. Origin, development and evolution of structural styles, in: Glennie, K.W. (Ed.), Petroleum Geology of the North Sea. Blackwell Science Ltd, Oxford, pp. 42–84.

Gluyas, J., Bowman, M., 1997. Edale no. 1 oilwell, Derbyshire, UK, 1938. Marine and Petroleum Geology 14, 191–199. https://doi.org/10.1016/S0264-8172(96)00066-9

Grantham, P.J., Posthuma, J., de Groot, K., 1980. Variation and significance of the C27 and C28 triterpane content of a North Sea core and various North Sea crude oils. Physics and Chemistry of the Earth 12, 29–38. https://doi.org/10.1016/0079-1946(79)90086-7

Gross, D., Sachsenhofer, R.F., Bechtel, A., Pytlak, L., Rupprecht, B., Wegerer, E., 2015. Organic geochemistry of Mississippian shales (Bowland Shale Formation) in central Britain: Implications for depositional environment, source rock and gas shale potential. Marine and Petroleum Geology 59, 1–21. https://doi.org/10.1016/j.marpetgeo.2014.07.022

Haarhoff, M.Q., Hughes, F., Heath-Clarke, M., Harrison, D., Taylor, C., Ware, D.L., Emms, G.G., Mortimer, A., 2018. The history of hydrocarbon exploration and development in North Yorkshire. Geological Society, London, Special Publications 465, 119–136. https://doi.org/10.1144/SP465.12

Han, J., Calvin, M., 1969. Hydrocarbon Distribution of Algae and Bacteria, and Microbiological Activity in Sediments. PNAS 64, 436–443. https://doi.org/10.1073/pnas.64.2.436

Hardy, N., 2011. Summary and conclusion report for 3D interpretation HEC. Internal ICL report, unpublished.

Heath-Clarke, M., Taylor, K., Harrison, D., Fogg, A., Hughes, F., Haarhoff, M., Mortimer, A., 2016. The characterization of unconventional reservoirs in the Bowland sequence using onshore 3D seismic data, Cleveland Basin, UK. First Break 34, 45–52.

Holba, A.G., Dzou, L.I.P., Hickey, J.J., Franks, S.G., May, S.J., Lenney, T., 1996. Reservoir geochemistry of South Pass 61 Field, Gulf of Mexico: compositional heterogeneities reflecting filling history and biodegradation. Organic Geochemistry, Reservoir and Production Geochemistry 24, 1179–1198. https://doi.org/10.1016/S0146-6380(96)00101-5

915 Holliday, D.W., 1999. Palaeotemperatures, thermal modelling and depth of burial studies in northern
916 and eastern England. Proceedings of the Yorkshire Geological and Polytechnic Society 52,
917 337–352. https://doi.org/10.1144/pygs.52.4.337
918 Holmes, R., 1991. Some aspects of the geology of the potash seam at Boulby Mine. Journal of the
919 Open University Geological Society 12, 77–88.
920 Huc, A.Y., Irwin, H., Schoell, M., 1985. Organic matter quality changes in an Upper Jurassic shale
921 sequence from the Viking Graben, in: Thomas, B.M. (Ed.), Petroleum Geochemistry in
922 Exploration of the Norwegian Shelf. Springer Netherlands, pp. 179–183.
923 Hughes, F., Harrison, D., Haarhoff, M., Howlett, P., Pearson, A., Ware, D., Taylor, C., Emms, G.,
924 Mortimer, A., 2018. The unconventional Carboniferous reservoirs of the Greater Kirby
925 Misperton gas field and their potential: North Yorkshire's sleeping giant. Geological Society,
926 London, Petroleum Geology Conference series 8, 611. https://doi.org/10.1144/PGC8.5
927 Husmo, T., Hamar, G.P., Høiland, O., Johannessen, E.P., Rømuld, A., Spencer, A., Titterton, R., 2002.
928 Lower and Middle Jurassic, in: Evans, D., Graham, C., Armour, A., Bathurst, P. (Eds.), The
929 Millenium Atlas: Petroleum Geology of the Central and Northern North Sea. Geological
930 Society of London, London, pp. 129–155.
931 Imber, J., Armstrong, H., Clancy, S., Daniels, S., Herringshaw, L., McCaffrey, K., Rodrigues, J.,
932 Trabucho-Alexandre, J., Warren, C., 2014. Natural fractures in a United Kingdom shale
933 reservoir analog, Cleveland Basin, northeast England natural fractures, Cleveland Basin.
934 AAPG Bulletin 98, 2411–2437. https://doi.org/10.1306/07141413144
935 Jiamo, F., Guoying, S., Pingan, P., Brassell, S.C., Eglinton, G., Jigang, J., 1986. Peculiarities of salt lake
936 sediments as potential source rocks in China. Organic Geochemistry 10, 119–126.
937 https://doi.org/10.1016/0146-6380(86)90015-X
938 Jiang, Z., Philp, R.P., Lewis, C.A., 1988. Fractionation of biological markers in crude oils during
939 migration and the effects on correlation and maturation parameters. Organic Geochemistry
940 13, 561–571. https://doi.org/10.1016/0146-6380(88)90076-9
941 Johnson, G.A.L., Somerville, I.D., Tucker, M.E., Cózar, P., 2011. Carboniferous stratigraphy and
942 context of the Seal Sands No. 1 Borehole, Teesmouth, NE England: the deepest onshore
943 borehole in Great Britain. Proceedings of the Yorkshire Geological Society 58, 173.
944 https://doi.org/10.1144/pygs.58.3.231
945 Jones, J.G., 1969. Studies on lipids of soil micro-organisms with particular reference to hydrocarbons.
946 Microbiology, 59, 145–152. https://doi.org/10.1099/00221287-59-2-145
947 Kara-Gülbay, R., Korkmaz, S., 2008. Organic geochemistry, depositional environment and
948 hydrocarbon potential of the Tertiary oil shale deposits in NW Anatolia, Turkey. Oil Shale 25,
949 444–464.
950 Kemp, S.J., Merriman, R.J., Bouch, J.E., 2005. Clay mineral reaction progress – the maturity and burial
951 history of the Lias Group of England and Wales. Clay Minerals 40, 43–61.
952 https://doi.org/10.1180/0009855054010154
953 Kent, P.E., 1980. Subsidence and uplift in east Yorkshire and Lincolnshire: a double inversion.
954 Proceedings of the Yorkshire Geological Society 42, 505–524.
955 https://doi.org/10.1144/pygs.42.4.505
956 Killops, S.D., Woolhouse, A.D., Weston, R.J., Cook, R.A., 1994. A geochemical appraisal of oil
957 generation in the Taranaki Basin, New Zealand. AAPG Bulletin 78, 1560–1585.
958 Kombrink, H., Besly, B., Collinson, J., den Hartog Jager, D., Drozdzewski, G., Dusar, M., Hoth, P.,
959 Pagnier, H., Stemmerik, L., Waksmnundzka, M., Wrede, V., 2010. Carboniferous, in:
960 Doornenbal, H., Stevenson, A. (Eds.), Petroleum Geological Atlas of the Southern Permian
961 Basin Area. EAGE Publications b.v. (Houten), pp. 81–99.
962 Mackenzie, A.S., Hoffmann, C.F., Maxwell, J.R., 1981. Molecular parameters of maturation in the
963 Toarcian shales, Paris Basin, France—III. Changes in aromatic steroid hydrocarbons.
964 Geochimica et Cosmochimica Acta 45, 1345–1355. https://doi.org/10.1016/0016-
965 7037(81)90227-1

966 Mackenzie, A.S., Mackenzie, A.S., 1984. Applications of biological markers in petroleum
967 geochemistry, in: Brooks, J., Welte, D. (Eds.), Advances in Petroleum Geochemistry.
968 Academic Press, London, pp. 115–214. https://doi.org/10.1016/B978-0-12-032001-1.50008-
969 0
970 Mackenzie, A.S., Maxwell, J.R., Coleman, M.L., Deegan, C.E., 1983. Biological marker and isotope
971 studies of North Sea crude oils and sediments, in: WPC-20104. Presented at the 11th World
972 Petroleum Congress, Proceedings of the 11th World Petroleum Congress, Geology
973 Exploration Reserves, WPC, pp. 45–56.
974 Mackenzie, A.S., Patience, R.L., Maxwell, J.R., Vandenbroucke, M., Durand, B., 1980. Molecular
975 parameters of maturation in the Toarcian shales, Paris Basin, France—I. Changes in the
976 configurations of acyclic isoprenoid alkanes, steranes and triterpanes. Geochimica et
977 Cosmochimica Acta 44, 1709–1721. https://doi.org/10.1016/0016-7037(80)90222-7
978 Mello, M.R., Telnaes, N., Gaglianone, P.C., Chicarelli, M.I., Brassell, S.C., Maxwell, J.R., 1988. Organic
979 geochemical characterisation of depositional palaeoenvironments of source rocks and oils in
980 Brazilian marginal basins. Organic Geochemistry 13, 31–45. https://doi.org/10.1016/0146-
981 6380(88)90023-X
982 Milsom, J., Rawson, P.F., 1989. The Peak Trough – a major control on the geology of the North
983 Yorkshire coast. Geological Magazine 126, 699–705.
984 https://doi.org/10.1017/S0016756800007007
985 Moldowan, J.M., Lee, C.Y., Watt, D.S., Jeganathan, A., Slougui, N.-E., Gallegos, E.J., 1991. Analysis and
986 occurrence of C26-steranes in petroleum and source rocks. Geochimica et Cosmochimica
987 Acta 55, 1065–1081. https://doi.org/10.1016/0016-7037(91)90164-Z
988 Moldowan, J.M., Seifert, W.K., Gallegos, E.J., 1985. Relationship between petroleum composition
989 and depositional environment of petroleum source rocks. AAPG Bulletin 69, 1255–1268.
990 Palacas, J.G., Anders, D.E., King, J.D., 1984. South Florida Basin—A prime example of carbonate
991 source rocks of petroleum, in: Palacas, J.G. (Ed.), Petroleum Geochemistry and Source Rock
992 Potential of Carbonate Rocks. AAPG Studies in Geology 18, pp. 71–96.
993 https://doi.org/10.1306/St18443C6
994 Parnell, J., 1988. Lacustrine petroleum source rocks in the Dinantian Oil Shale Group, Scotland: a
995 review. Geological Society, London, Special Publications 40, 235–246.
996 https://doi.org/10.1144/GSL.SP.1988.040.01.20
997 Peters, K.E., Moldowan, J.M., 1991. Effects of source, thermal maturity, and biodegradation on the
998 distribution and isomerization of homohopanes in petroleum. Organic Geochemistry 17, 47–
999 61. https://doi.org/10.1016/0146-6380(91)90039-M
1000 Peters, K.E., Moldowan, J.M., Driscole, A.R., Demaison, G.J., 1989. Origin of Beatrice oil by co-
1001 sourcing from Devonian and Middle Jurassic source rocks, Inner Moray Firth, United
1002 Kingdom. AAPG Bulletin 73, 454–471.
1003 Peters, K.E., Walters, C.C., Moldowan, J.M., 2005. The Biomarker Guide. Biomarkers and Isotopes in
1004 Petroleum Exploration and Earth History vol. 2. Cambridge University Press, Cambridge,
1005 1155p. https://doi.org/10.1017/CBO9781107326040
1006 Petersen, H.I., Hertle, M., Juhasz, A., Krabbe, H., 2016. Oil family typing, biodegradation and source
1007 rock affinity of liquid petroleum in the Danish North Sea. Journal of Petroleum Geology 39,
1008 247–268. https://doi.org/10.1111/jpg.12645
1009 Pletsch, T., Appel, J., Botor, D., Clayton, C., Duin, E., Faber, E., Górecki, W., Kombrink, H., Kosakowski,
1010 P., Kuper, G., Kus, J., Lutz, R., Mathiesen, A., Ostertag-Henning, C., Papiernik, B., Bergen, F.,
1011 2010. Petroleum generation and migration, in: Doornenbal, H., Stevenson, A. (Eds.),
1012 Petroleum Geological Atlas of the Southern Permian Basin Area. EAGE Publications b.v.
1013 (Houten), pp. 225–253.
1014 Powell, J.H., 2010. Jurassic sedimentation in the Cleveland Basin: a review. Proceedings of the
1015 Yorkshire Geological Society 58, 21–72. https://doi.org/10.1144/pygs.58.1.278
1016 Rawson, P.F., Wright, J.K., 2018. The Yorkshire coast, 4th ed. Geologists' Association Guides 34, 178p.

Rawson, P.F., Wright, J.K., 1995. Jurassic of the Cleveland Basin, North Yorkshire, in: Taylor, P.D. (Ed.), Field Geology of the British Jurassic. Geological Society, London, pp. 173–208.

Requejo, A.G., Allan, J., Creaney, S., Gray, N.R., Cole, K.S., 1992. Aryl isoprenoids and diaromatic carotenoids in Paleozoic source rocks and oils from the Western Canada and Williston Basins. Organic Geochemistry 19, 245–264. https://doi.org/10.1016/0146-6380(92)90041-U

Scotchman, I.C., 1991. Kerogen facies and maturity of the Kimmeridge Clay Formation in southern and eastern England. Marine and Petroleum Geology 8, 278–295. https://doi.org/10.1016/0264-8172(91)90082-C

Seifert, W.K., Moldowan, J.M., 1980. The effect of thermal stress on source-rock quality as measured by hopane stereochemistry. Physics and Chemistry of the Earth 12, 229–237. https://doi.org/10.1016/0079-1946(79)90107-1

Seifert, W.K., Moldowan, J.M., 1979. The effect of biodegradation on steranes and terpanes in crude oils. Geochimica et Cosmochimica Acta 43, 111–126. https://doi.org/10.1016/0016-7037(79)90051-6

Seifert, W.K., Moldowan, J.M., 1978. Applications of steranes, terpanes and monoaromatics to the maturation, migration and source of crude oils. Geochimica et Cosmochimica Acta 42, 77–95. https://doi.org/10.1016/0016-7037(78)90219-3

Shanmugam, G., 1985. Significance of coniferous rain forests and related organic matter in generating commercial quantities of oil, Gippsland Basin, Australia. AAPG Bulletin 69, 1241–1254.

Shen, G., Fan, S., Lin, D., Su, N., Zhou, H., 1980. The geochemistry of n-alkanes with an even-odd predominance in the Tertiary Shahejie Formation of northern China. Physics and Chemistry of the Earth, Proceedings of the Ninth International Meeting on Organic Geochemistry 12, 115–121. https://doi.org/10.1016/0079-1946(79)90093-4

Simoneit, B.R.T., 1977. Diterpenoid compounds and other lipids in deep-sea sediments and their geochemical significance. Geochimica et Cosmochimica Acta 41, 463–476. https://doi.org/10.1016/0016-7037(77)90285-X

Sinninghe Damsté, J.S., Kenig, F., Koopmans, M.P., Köster, J., Schouten, S., Hayes, J.M., de Leeuw, J.W., 1995. Evidence for gammacerane as an indicator of water column stratification. Geochimica et Cosmochimica Acta 59, 1895–1900. https://doi.org/10.1016/0016-7037(95)00073-9

Sinninghe Damsté, J.S., Schouten, S., van Duin, A.C.T., 2001. Isorenieratene derivatives in sediments: possible controls on their distribution. Geochimica et Cosmochimica Acta 65, 1557–1571. https://doi.org/10.1016/S0016-7037(01)00549-X

Sinninghe Damsté, J.S., Wakeham, S.G., Kohnen, M.E.L., Hayes, J.M., de Leeuw, J.W., 1993. A 6,000–year sedimentary molecular record of chemocline excursions in the Black Sea. Nature 362, 827–829. https://doi.org/10.1038/362827a0

Słama, S., 2019. Chemical characteristics and origin of crude oil from the Boulby Mine (NE England) based on analysis of the saturated hydrocarbon fraction. BSc thesis, University of Warsaw, 42p.

Słowakiewicz, M., 2016. Characteristic biomarkers in organic matter from three Zechstein (Late Permian) carbonate units. Zeitschrift der Deutschen Gesellschaft für Geowissenschaften 167, 269–279. https://doi.org/10.1127/zdgg/2016/0061

Słowakiewicz, M., Blumenberg, M., Więcław, D., Röhling, H.-G., Scheeder, G., Hindenberg, K., Leśniak, A., Idiz, E.F., Tucker, M.E., Pancost, R.D., Kotarba, M.J., Gerling, J.P., 2018. Zechstein Main Dolomite oil characteristics in the Southern Permian Basin: I. Polish and German sectors. Marine and Petroleum Geology 93, 356–375. https://doi.org/10.1016/j.marpetgeo.2018.03.023

Słowakiewicz, M., Gąsiewicz, A., 2013. Palaeoclimatic imprint, distribution and genesis of Zechstein Main Dolomite (Upper Permian) petroleum source rocks in Poland: Sedimentological and

1067 geochemical rationales. Geological Society, London, Special Publications 376, 523–538.
1068 https://doi.org/10.1144/SP376.21
1069 Słowakiewicz, M., Tucker, M.E., Hindenberg, K., Mawson, M., Idiz, E.F., Pancost, R.D., 2016.
1070 Nearshore euxinia in the photic zone of an ancient sea: Part II – The bigger picture and
1071 implications for understanding ocean anoxia. Palaeogeography, Palaeoclimatology,
1072 Palaeoecology 461, 432–448. https://doi.org/10.1016/j.palaeo.2016.09.003
1073 Słowakiewicz, M., Tucker, M.E., Vane, C.H., Harding, R., Collins, A., Pancost, R.D., 2015. Shale-gas
1074 potential of the mid-Carboniferous Bowland-Hodder unit in the Cleveland Basin (Yorkshire)
1075 Central Britain. Journal of Petroleum Geology 38, 59–75. https://doi.org/10.1111/jpg.12598
1076 Smith, D.B., 1989. The late Permian palaeogeography of north-east England. Proceedings of the
1077 Yorkshire Geological and Polytechnic Society 47, 285–312.
1078 https://doi.org/10.1144/pygs.47.4.285
1079 Smith, D.B., Francis, E.A., 1967. Permian and Trias, in: Smith, D.B., Francis, E.A., Calver, M.A., Gaunt,
1080 G.D., Pattison, J., Edwards, A.H., Harrison, R.K. (Eds.), Geology of the Country between
1081 Durham and West Hartlepool, Memoirs of the Geological Survey of Great Britain, England
1082 and Wales. pp. 90–186.
1083 Smith, D.B., Harwood, G.M., Pattison, J., Pettigrew, T.H., 1986. A revised nomenclature for Upper
1084 Permian strata in eastern England. Geological Society, London, Special Publications 22, 9–17.
1085 https://doi.org/10.1144/GSL.SP.1986.022.01.02
1086 Smith, K., Smith, N.J.P., Holliday, D.W., 1985. The deep structure of Derbyshire. Geological Journal 20,
1087 215–225. https://doi.org/10.1002/gj.3350200303
1088 Sofer, Z., 1984. Stable carbon isotope compositions of crude oils; application to source depositional
1089 environments and petroleum alteration. AAPG Bulletin 68, 31–49.
1090 Song, J., 2015. Shale oil potential and depositional environment of the Lower Toarcian Posidonia
1091 Shale in NW Europe. Publikationsserver der RWTH Aachen University.
1092 Song, J., Littke, R., Weniger, P., Ostertag-Henning, C., Nelskamp, S., 2015. Shale oil potential and
1093 thermal maturity of the Lower Toarcian Posidonia Shale in NW Europe. International Journal
1094 of Coal Geology 150–151, 127–153. https://doi.org/10.1016/j.coal.2015.08.011
1095 Steele, R.P., 1983. Longitudinal draa in the Permian Yellow Sands of North-East England, in:
1096 Brookfield, M.E., Ahlbrandt, T.S. (Eds.), Developments in Sedimentology. Elsevier, pp. 543–
1097 550. https://doi.org/10.1016/S0070-4571(08)70812-4
1098 Summons, R.E., Powell, T.G., 1986. Chlorobiaceae in Palaeozoic seas revealed by biological markers,
1099 isotopes and geology. Nature 319, 763–765. https://doi.org/10.1038/319763a0
1100 Sun, Y., Sheng, G., Peng, P., Fu, J., 2000. Compound-specific stable carbon isotope analysis as a tool
1101 for correlating coal-sourced oils and interbedded shale-sourced oils in coal measures: an
1102 example from Turpan basin, north-western China. Organic Geochemistry 31, 1349–1362.
1103 https://doi.org/10.1016/S0146-6380(00)00069-3
1104 Taylor, J.C.M., 1998. Upper Permian - Zechstein, in: Glennie, K.W. (Ed.), Petroleum Geology of the
1105 North Sea. Blackwell Science Ltd, pp. 174–211.
1106 Ten Haven, H.L., De Leeuw, J.W., Schenck, P.A., 1985. Organic geochemical studies of a Messinian
1107 evaporitic basin, northern Apennines (Italy) I: Hydrocarbon biological markers for a
1108 hypersaline environment. Geochimica et Cosmochimica Acta 49, 2181–2191.
1109 https://doi.org/10.1016/0016-7037(85)90075-4
1110 Thompson, K.F.M., 1987. Fractionated aromatic petroleums and the generation of gas-condensates.
1111 Organic Geochemistry 11, 573–590. https://doi.org/10.1016/0146-6380(87)90011-8
1112 Thompson, K.F.M., 1983. Classification and thermal history of petroleum based on light
1113 hydrocarbons. Geochimica et Cosmochimica Acta 47, 303–316.
1114 https://doi.org/10.1016/0016-7037(83)90143-6
1115 Underhill, J.R., 2003. The tectonic and stratigraphic framework of the United Kingdom's oil and gas
1116 fields. Geological Society, London, Memoirs 20, 17–59.
1117 https://doi.org/10.1144/GSL.MEM.2003.020.01.04

Underhill, J.R., Monaghan, A.A., Browne, M.A.E., 2008. Controls on structural styles, basin development and petroleum prospectivity in the Midland Valley of Scotland. Marine and Petroleum Geology 25, 1000–1022. https://doi.org/10.1016/j.marpetgeo.2007.12.002

van Buchem, F.S.P., Knox, R.W.OB., 1998. Lower and Middle Liassic Depositional Sequences of Yorkshire (U.K.), in: Graciansky, P.-C. de, Hardenbol, J., Jacquin, T., Vail, P.R. (Eds.), Mesozoic and Cenozoic Sequence Stratigraphy of European Basins. SEPM Special Publication, pp. 545–559. https://doi.org/10.2110/pec.98.02.0545

van Kaam-Peters, H.M.E., Schouten, S., de Leeuw, J.W., Sinninghe Damsté, J.S., 1997. A molecular and carbon isotope biogeochemical study of biomarkers and kerogen pyrolysates of the Kimmeridge Clay Facies: palaeoenvironmental implications. Organic Geochemistry 27, 399–422. https://doi.org/10.1016/S0146-6380(97)00084-3

Walters, C.C., Lillis, P.G., Peters, K.E., 2012. Molecular indicators of geothermal history, in: Harris, N.B., Peters, Kenneth E. (Eds.), Analyzing the Thermal History of Sedimentary Basins: Methods and Case Studies, SEPM Special Publication. Tulsa, pp. 17–28. https://doi.org/10.2110/sepmsp.103

Waples, D.W., Machihara, R., 1991. Biomarkers for geologists: a practical guide to the application of steranes and triterpanes in petroleum geology, AAPG Methods in Exploration Series 9, 91p.

Wenger, L.M., Davis, C.L., Isaksen, G.H., 2002. Multiple controls on petroleum biodegradation and impact on oil quality. SPE Reservoir Evaluation & Engineering 5, 375–383. https://doi.org/10.2118/80168-PA

Woods, P.J.E., 1979. The geology of Boulby Mine. Economic Geology 74, 409–418. https://doi.org/10.2113/gsecongeo.74.2.409

Woods, P.J.E., 1973. Potash exploration in Yorkshire: Boulby Mine pilot borehole. Transactions of the Institute of Minerals and Metallurgical Transactions 82B, 99–106.

Sample no	C_{27} Ts/Tm	M/H	C_{29} 20S	C_{29} ββ	TA(I)/ TA(I+II)	MPI 1	Rc	MDR	Rm
1	0.41	0.12	0.52	0.56	0.07	0.65	0.79	4.88	0.87
2	nd	nd	nd	nd	nd	1.39	1.23	nd	nd
3	nd	nd	nd	nd	nd	1.3	1.18	nd	nd
4	nd	nd	nd	nd	nd	1.33	1.2	nd	nd
Malton 4	0.52-0.71 (0.6)	0.03-0.13 (0.07)	0.46-0.57 (0.51)	0.45-0.58 (0.51)	0.25-0.33 (0.29)	0.7-0.81 (0.75)	0.7-0.81 (0.75)	1.78-2.02 (1.9)	0.64-0.66 (0.65)

Table 1. Biomarker and non-biomarker maturity parameters for Boulby oil (samples 1-4) and Malton 4 KAF samples. nd – not determined. Numerator gives range of values and denominator gives average values.

C_{27} Ts/Tm – C_{27} 18α-trisnorneohopane/17α-trisnorhopane

M/H – moretane/hopane

C_{29} 20S – 20S/(20S + 20R) epimers of 5α(H),14α(H),17α(H)-ethylsterane

C_{29} ββ – 5α(H),14β(H),17β(H)/[5α(H),14β(H),17β(H) + 5α(H),14α(H),17α(H) 20R ethylsteranes]

TA(I)/TA(I + II) – TA(I) = C_{20} + C_{21}, TA(II)=ΣC_{26}-C_{28} (20S + 20R) triaromatic steroids

MPI 1 – methylphenanthrene index = 1.5 × (2-MP + 3-MP)/P + 1-MP + 9-MP

Rc – calculated vitrinite reflectance = 0.40 + 0.60 × MPI 1

MDR – methyldibenzothiophene ratio = 4-MDBT/1-MDBT

R_m – calculated vitrinite reflectance = 0.073 × MDR + 0.51

Sample	density [g/cm^3]	$\delta^{13}C_{SAT}$	$\delta^{13}C_{ARO}$	CV
1	0.84617	-25.2	-24.4	-2.06
2	0.80984	-24.25	-22.61	-0.49
3	0.84487	-24.04	-22.58	-0.96
4	0.81543	-23.92	-23.37	-3.01

Table 2. Density and stable carbon isotopic composition of the saturated ($\delta^{13}C_{SAT}$, ‰) and aromatic ($\delta^{13}C_{ARO}$, ‰) fractions of Boulby oil (samples 1-4). CV – canonical variable (CV = $-2.53\delta^{13}C_{SAT}$ + $2.22\delta^{13}C_{ARO}$ – 11.65; after Sofer, 1984).

Sample no	Pr/Ph	Pr/*n*-C_{17}	Ph/*n*-C_{18}	C_{19}/C_{23}	C_{24Tet}/C_{23}	C_{29}/H	C_{30dia}/H	C_{31}R/H
1	0.71	0.54	0.78	0.07	0.07	0.27	0.09	0.39
2	0.71	0.27	0.53	nd	nd	nd	nd	nd

3	0.72	0.28	0.54	nd	nd	nd	nd	nd
4	0.71	0.28	0.54	nd	nd	nd	nd	nd
Malton 4	$\frac{0.3-0.46}{(0.38)}$	$\frac{0.17-0.58}{(0.42)}$	$\frac{0.21-0.58}{(0.51)}$	$\frac{0.03-0.24}{(0.08)}$	$\frac{0.14-0.58}{(0.31)}$	$\frac{0.49-1.17}{(0.74)}$	nd	$\frac{0.31-0.52}{(0.4)}$

1174

1175 Table 3a. Source-related geochemical characteristics of Boulby oil (samples 1-4) and Malton 4
1176 dolomite samples. nd – not determined. Numerator gives range of values and denominator gives
1177 average values.

1178

HHI	$C_{32(S+R)}/C_{31(S+R)}$	$C_{34(S+R)}/C_{33(S+R)}$	$C_{35}S/C_{34}S$	C_{27}dia	C_{29}dia	$\%C_{27}$	$\%C_{28}$
0.14	1.3	1.35	0.8	0.33	0.69	39	25
nd	nd	nd	nd	0.49	nd	13	nd
nd	nd	nd	nd	0.72	nd	12	nd
nd	nd	nd	nd	0.94	nd	9	nd
$\frac{0.09-0.3}{(0.21)}$	$\frac{0.82-1.43}{(1.02)}$	$\frac{0.63-1.88}{(0.98)}$	$\frac{0.45-1.79}{(1.23)}$	$\frac{0.75-4.33}{(1.7)}$	$\frac{0.28-2.48}{(0.77)}$	$\frac{31-44}{(38)}$	$\frac{24-27}{(26)}$

1179

1180 Table 3b. Continued.

1181

$\%C_{29}$	C_{27}/C_{29}	C_{28}/C_{29}	tricyclics/17α-hopanes	steranes/17α-hopanes	DBT/P	CPI
36	1.09	0.871	0.03	0.25	0.49	0.98
87	nd	nd	nd	nd	0.36	0.99
88	nd	nd	nd	nd	0.42	1.02
91	nd	nd	nd	nd	0.26	0.99
$\frac{29-42}{(36)}$	$\frac{0.75-1.53}{(1.08)}$	$\frac{0.6-0.91}{(0.72)}$	$\frac{0.14-1.19}{(0.67)}$	$\frac{0.12-0.37}{(0.23)}$	$\frac{0.86-1.34}{(1.16)}$	$\frac{0.83-1.01}{(0.95)}$

1182

1183 Table 3c. Continued.

1184

1185 Pr/Ph – pristane/phytane.
1186 Pr/*n*-C_{17} – pristane/*n*-heptadecane.
1187 Ph/*n*-C_{18} – phytane/*n*-octadecane.
1188 C_{19}/C_{23} – C_{19}/C_{23} tricyclic terpanes.
1189 C_{22}/C_{21} – C_{22}/C_{21} tricyclic terpanes.

C_{24Tet}/C_{23} – C_{24} tetracyclic/C_{23} tricyclic terpanes.

C_{29}/H – C_{29} norhopane/C_{30} 17α-hopane.

C_{30} dia/H – C_{30} diahopane/C_{30} 17α-hopane.

C_{31} R/H – C_{31} homohopane 22R/C_{30} 17α-hopane.

HHI – homohopane index: $C_{35}\alpha\beta(S + R)/(\Sigma C_{31}\text{-}C_{35}\alpha\beta\ S + R)$.

C_{32}/C_{31} (S + R) – C_{32} (S + R) 17α-hopane/C_{31} (S + R) 17α-hopane.

C_{34}/C_{33} (S + R) – C_{34} (S + R) 17α-hopane/C_{33} (S + R) 17α-hopane.

$C_{35}S/C_{34}S$ - $C_{35}S/C_{34}S$ homohopanes.

C_{27} dia – diasterane/sterane ratio – C_{27} 13β,17α(H) (20S + 20R)/(C_{27} 5α,14α,17α(H) 20S + 20R + 5α,14β,17β(H) 20S + 20R).

C_{29} dia – diasterane/sterane ratio – C_{29} 13β,17α(H) (20S + 20R)/(C_{29} 5α,14α,17α(H) 20S + 20R + 5α,14β,17β(H) 20S + 20R).

%C_{27} (*m*/*z* 217) – 100 × $C_{27}S/(C_{27}S + C_{28}S + C_{29}S)$.

%C_{28} (*m*/*z* 217) – 100 × $C_{28}S/(C_{27}S + C_{28}S + C_{29}S)$.

%C_{29} (*m*/*z* 217) – 100 × $C_{29}S/(C_{27}S + C_{28}S + C_{29}S)$.

C_{27}/C_{29} – C_{27}/C_{29} sterane ratio.

C_{28}/C_{29} – C_{28}/C_{29} sterane ratio.

Tricyclics/17α-hopanes – $\Sigma C_{19\text{-}26}$ tricylic terpanes/($\Sigma C_{19\text{-}26}$ tricylic terpanes + $\Sigma C_{29\text{-}35}$ 17α-hopanes).

Steranes/17α-hopanes – $\Sigma C_{27\text{-}29}$ regular steranes/$\Sigma C_{29\text{-}35}$ 17α-hopanes.

DBT/P – dibenzothiophene/phenanthrene.

CPI – carbon preference index based on *n*-alkanes [$\Sigma(C_{25}\text{-}C_{33})$odd/$\Sigma(C_{24}\text{-}C_{32})$even + $\Sigma(C_{25}\text{-}C_{33})$odd/$\Sigma(C_{26}\text{-}C_{34})$even]/2.

Highlights

- A new and working petroleum source rock on the UK Continental Shelf
- Boulby oil seeping from rock-salt fractures derives from sapropelic dolomite
- A carbonate-evaporite depositional setting is confirmed

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: